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U.S.--Canada Memorandum of Intent on Transboundary Air Pollution. Impact Assessment

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ON
TRANSBOUNDARY AIR POLLUTION

IMPACT ASSESSMENT
INTERIM REPORT
FEBRUARY 1981

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16. ABSTRACT

This is an Interim Report prepared by a US/Canada Work Group in accordance with the Memorandum of Intent on Transboundary Air Pollution concluded between Canada and the United States on August 5, 1980.

This is one of a set of four reports which represent an initial effort to draw together currently available information on transboundary air pollution, with particular emphasis on acid deposition, and to develop a consensus on the nature of the problem and the measures available to deal with it. While these reports contain some information and analyses that should be considered prelimainary in nature, the accurately reflect the current state of knowledge on the issures considered. Any portion of these reports is subject to modification and refinement as peer review, further advances in scientific understanding, or the results of ongoing assessment studies become available.

Other Transboundary air pollution will also be included.

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This is an Interim Report prepared by a U.S./Canada Work Group in accordance with the Memorandum of Intent on Transboundary Air Pollution concluded between Canada and the United States on August 5, 1980.

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More complete reports on acid deposition are expected in mid 1981 and early 1982. Other transboundary air pollution issues will also be included in these reports.

February 2, 1981
(revised February 10, 1981)

TO: Co-Chairmen
Canada/United States
Co-ordinating Committee

FROM: Co-Chairmen
Impact Assessment Work Group

In accordance with the approved work plan for the Impact Assessment Work Group, we are transmitting the required January 15 Interim Report.

The draft Interim Report was submitted to Work Group 3A on December 18, 1980 for their comments, especially as related to policy direction. The draft has also undergone considerable scrutiny and review by members of WG-1.

Members of WG-1 have made an effort, under very tight time constraints, to produce a useful product for the Co-ordinating Committee. We must caution the committee, however, that the findings and conclusions of the report must be regarded as preliminary. This is an Interim Report which needs careful review by the scientific community. We expect to improve and strengthen this report considerably during Phase II through the addition of new information, improved organization of the material and extensive peer review.

We look forward to your comments and further direction.

Respectfully submitted,

Barry R. Flamm

B.R. Flamm
United States Co-Chairman

G.E. Bangay
Canadian Co-Chairman

WORK GROUP 1

IMPACT ASSESSMENT

INTERIM REPORT

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PREFACE

In August, 1980, the Governments of Canada and the United States signed a Memorandum of Intent concerning transboundary air pollution. This action was taken in response to concern for actual and potential damage resulting from the long-range transport of air pollutants between countries and in recognition of the already serious problem of acid rain.

Each country has demonstrated concern for the causing of damage to the other's environment by transboundary movement of their pollutants. This concern is rooted in international agreements, such as the 1909 Boundary Waters Treaty, the Great Lakes Water Quality Agreement, and the 1979 E.C.C. Convention on Long Range Transboundary Air Pollution, all of which both Canada and the United States have signed.

The Memorandum noted that both countries have set a priority on developing a scientific understanding of long-range transport of air pollutants and resulting environmental effects, and on developing and implementing policies and technologies to combat such effects.

To achieve the first steps of this overall objective, the memorandum established a plan of action for the period October, 1980 to January, 1982, during which time five documents are to be prepared by the following work groups:

1. Impact assessment
2. Atmospheric modelling of pollutant movements
3A. Strategies development and implementation
3B. Emissions, cost and engineering assessment
4. Legal, institutional arrangements and drafting (preparation of the actual document to be signed)

General terms of reference that apply to all work groups were established, together with detailed terms dealing with each work group.

General Terms of Reference (as per MOI)

1. The Work Groups shall function under the general direction and policy guidance of a United States/Canada Coordinating Committee co-chaired by the Department of External Affairs and the Department of State.

2. The Work Groups shall provide reports assembling and analyzing information and identifying measures as outlined below, which will provide the basis of proposals for inclusion in a transboundary air pollution agreement. These reports shall be provided by January, 1982, and shall be based on available information.

3. Within one month of the establishment of the Work Groups, they shall submit to the United States/Canada Coordinating Committee a work plan to accomplish the specific tasks outlined below. Additionally, each Work Group shall submit an interim report by January 15, 1981.

4. During the course of negotiations, and under the general direction and policy of the Coordinating Committee, the Work Groups shall assist the Coordinating Committee as required.

5. Nothing in the foregoing shall preclude subsequent alterations of the tasks of the Work Groups or the establishment of additional Work Groups, as may be agreed upon by the Governments.

Specific Terms of Reference: Impact Assessment Work Group

The Group will provide information on the current, and projected impacts of air pollutants on sensitive receptor areas, and prepare proposals for the 'Research, Modelling and Monitoring' elements of an agreement.

In carrying out this work, the Group will:

1. identify and assess physical and biological consequences possibly related to transboundary air pollution;

2. determine the present status of physical and biological indicators, which characterize the ecological stability of each sensitive area identified;

3. review available data bases to establish historic adverse environmental impacts more accurately;

4. determine the current adverse environmental impact within identified sensitive areas--annual, seasonal, episodic;

5. determine the release of residues potentially related to transboundary air pollution, including possible episodic release from snowpack melt in sensitive areas;

6. assess the years remaining before significant ecological changes are sustained within identified sensitive areas;

7. propose reductions in the air pollutant deposition rates--annual, seasonal, episodic--which would be necessary to protect identified sensitive areas; and

8. prepare proposals for the 'Research, Modelling and Monitoring' elements of an agreement.

A time frame was established which called for a first draft of the impact asessment report by January, 1981, a second draft by May, 1981, and a final report by January, 1982.

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The Canada/United States Impact Assessment Work Group wishes to acknowledge the assistance of the numerous individuals and agencies involved in the various aspects of this study. The enthusiasm and dedication demonstrated especially under the extremely tight time constraints experienced in this first phase of the program were fundamental to the successful completion of this interim report. These persons included A. Anders (University of Wisconsin), R. Coote (Agriculture Canada), D. Cowell (Environment Canada), C. Cronan (University of Maine), R. Dilabio (Energy, Mines and Resources), L. Dochinger (U.S. Department of Agriculture), N. Foster (Environment Canada), M. Griffith (Ministry of the Environment), W. Hart (Environment Canada), M. Havas (University of Toronto), W. Heck (North Carolina State University), J. Jacobsen (Cornell University), D. Johnson (Oak Ridge National Laboratory), M. Kelly (Oak Ridge National Laboratory), J. Kramer, (McMaster University), O. Loucks (Institute of Ecology), A. Lucas (Environment Canada), W. McFee (Perdue University), I. Morrison (Environment Canada), J. Nicholson (Environment Canada), D. Raynal (State University of New York), C. Rubec (Environment Canada), C. Schofield (Cornell University), S. Singh (Agriculture Canada), D. Shriner (Oak Ridge National Laboratory).

SECTION 1
EXECUTIVE SUMMARY

Introduction

In this first phase of activities under the MOI, the Impact Assessment Work Group has concentrated its resources on identifying the key physical and biological impacts resulting from pollution associated with transboundary air movement. In the interim report the acid precipitation component has been emphasized but other important problems such as oxidants are identified where there is presently a well documented concern. Other aspects will be dealt with in the second phase.

Acid deposition is currently being observed in most of eastern North America. Within this half-continent are large areas in which the surface soil material and bedrock types have little buffering capacity for acid inputs and are identified as "potentially sensitive". These areas include some of the most unique, unspoiled and biologically productive environments in North America. The potential is high for environmental degradation from the deposition of acid and other pollutants.

During atmospheric transport of sulphur oxides (SO_x) and nitrogen oxides (NO_x) in large scale air mass movements, conversion to their acid components takes place. Measurements of the present level of chemical constituents in precipitation show that large areas of North America receive about 40 times more acid than normal*. This excessive loading is deposited in precipitation as wet fallout, and in, dry fallout, as dust particles, and in gaseous forms. Like some components of acid precipitation, ozone is a secondary pollutant, not being emitted directly, but formed in the atmosphere in the presence of sunlight as a result of chemical transformations of nitrogen dioxide and reactive hydrocarbons.

Terrestrial Effects

Ozone injury to vegetation and yield reductions have been well documented on many crop species in the eastern U.S. and Ontario. These crops include tobacco, white beans, soybeans, corn, potatoes, grapes, onion, cucumber, celery, pumpkin, squash and radish. At ambient concentrations of 0.05 to 0.10 ppm during continuous or intermittent exposure periods, loss of plant tissue may approach 15-30% and yield losses of 5-10% may occur for the most susceptible crops. Direct effects of acid precipitation, have been demonstrated under experimental conditions and may be of potential concern especially on crops for which the foliage is valued. Other potential impacts include: (1) damage to protective surface structures such a cuticle; (2) interference with normal functions of guard cells; (3) poisoning of plant cells after diffusion of acidic substances throug stomata or cuticle; (4) disturbance of normal metabolism or growth processes without necrosis of plant cells; (5) alteration of leaf an root-exudation processes; (6) interference with reproduction processes, and (7) synergistic interaction with other environmental stress factors.

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*For the purpose of this report, normal is considered to be the acidity of precipitation in equilibrium with background atmospheric conditions, or pH 5.6. It is recognized that varying natural conditions can result in a pH of rainfall higher or lower than this value.

An increase in soil acidity can be detrimental to the chemical availability of several essential macro nutrients and over decades we can expect a net loss of cations (Ca^{2+} and Mg^{2+}), important for plant growth, from poorly buffered sites. Areas with soils of low pH are characterized as having low base exchange conditions. In this situation, any further loss of cations is considered significant, however small that loss may be. Much of eastern Canada's forest industry is founded on these low pH soils. The general restriction of commercial forest production to "less productive" sites, coupled with new harvesting technology (where more of the tree is removed from the site, thus reducing the availability of nutrients for recycling), and the tradition of not applying lime may increase the vulnerability of long term forest growth to acid precipitation.

An increase in soil acidity can also lead to mobilization of other elements (Al, Mn, Fe) sometimes in quantities toxic to terrestrial plants and to aquatic ecosystems. In fact, some studies have indicated that mass mortalities of fish, observed during transient episodes of acidification in the spring, are most likely a result of elevated levels of inorganic aluminum mobilized from the soils by strong acids present in snowmelt water.

The terrestrial systems influence on the acid component of precipitation also has important implications for the aquatic ecosystem. The results presented in this report on the mobility of nitrate and ammonium ions have shown that most of the nitrogen added to the watershed is retained by growing plants where it can be beneficial if it is in limited supply. In cases where sulphate is limiting for plant growth atmospheric deposition can be beneficial, however, following a period of sulphate saturation in soils, most of the sulphur passes through to the aquatic system. Thus, it appears that control of sulphur deposition would be more effective in reducing the rate of acidification of surface waters than control of nitrogen inputs.

Aquatic Effects

The impact of acid deposition on water quality and the aquatic ecosystem is better quantified and understood than that on terrestrial ecosystems. There are a number of examples where dramatic changes in water quality believed to be directly attributable to acid precipitation, have occurred. In Nova Scotia, comparisons of recent data with results from the mid-1950s show decreases in pH and concurrent increases in excess sulphate loads. At present, there are 9 rivers in this province with a pH of 4.7 which no longer support salmon or trout reproduction; 11 rivers are in the pH range 4.7-5.0 where some juvenile salmon mortality is probably occurring; and 7 rivers are in the pH range 5.1-5.3, which is considered borderline for Atlantic salmon. If current acid loadings continue, it appears probable that more of the inland and Atlantic salmon fisheries in Canada will be lost.

A similar 17-year trend toward acidification of some headwater streams has been observed in New Jersey. In addition, high elevation lakes in the Adirondacks have shown a marked pH decline over a 40 year period. This is one of the most sensitive lake districts in the eastern United States. A recent inventory has indicated that at least 180 former brook trout ponds will no longer support trout because of acidification.

A summary of several Canadian lake studies supports the conclusion that acidic precipitation has reduced the alkalinity of surface water in many lakes, thus increasing their vulnerability to continued acid deposition. Many of the affected lakes are not technically acidified (in the sense of depressed pH), but the long-term biological consequences of the altered water chemistry are unknown at this time. Although naturally acid lakes do occur, the significant number of seriously acidified lakes appears to be a recent response of low alkalinity systems to the continuing addition of H^+ and SO_4^{2-}.

Concurrent with negative impacts on the fishery, there have been changes in other components of the aquatic ecosystem. Acidification results in changes in the makeup, size and metabolism of plankton communities. These alterations hold important implications for other organisms higher in the food chain.

Many species of frogs, toads and salamanders breed in temporary pools which are susceptible to pH depression due to the rapid flushing of accumulated acid during spring snowmelt.

Field surveys in North America and Europe have documented the sensitivity of amphibians to depressed pH and the decreases in their numbers, especially those inhabiting temporary pools. The danger that they may become locally extinct, and their significance in the food chain, hold important implications for other wildlife.

Health Effects

Although available information gives little cause for concern over direct health effects from acid deposition, there are at least two indirect effects of concern: (1) contamination of edible fish by toxic materials, principally mercury; and (2) leaching and corrosion of watersheds and water storage and distribution systems, leading to elevated levels of toxic elements in drinking water supplies.

While the mechanisms are not fully understood, available data indicate that fish in poorly buffered lakes contain elevated mercury levels, some in excess of Canadian and United States action levels (0.5 mg/kg and 1.0 mg/kg respectively). Unrestricted consumption of fish containing mercury in excess of these action levels can lead to brain damage and neurological disorders in humans. No clear evidence exists, however, that such effects have resulted as a direct consequence of acidic precipitation.

A number of drinking water supplies have apparently become contaminated with metals as a result of acidic deposition, but no clear evidence of health effects from drinking these contaminated waters was reported. The elements most frequently detected were lead, cadmium, copper and zinc. In one Pennsylvania county, 16 per cent of cistern waters contained lead in excess of the United States and Canadian drinking water standards (50 mg/l). Populations at high risk include those obtaining drinking water from poorly buffered lakes and streams (or eating fish from such areas), and those using acidified groundwater or cisterns as a source of drinking water.

Visibility Effects

Effects of transboundary air pollution on visibility are related to air quality, not to acidic deposition. Acid precursors which can significantly affect visibility are sulphuric acid and various ammonium sulphate aerosols. Available data do not suggest that nitrates (predominantly in the vapour phase) play a significant role, but visible brown plumes from NO_2 have been reported at a distance of 100 km from isolated point sources.

From available information on background and incremental pollutant loadings and relative humidity, estimates of visibility impacts (reduction in visual range and contrast, discolouration from haze or plumes) can be made. Analysis of airport data indicate a substantial decline in regional summertime visibility, in eastern North America, between 1950 and 1974. This change may be associated with changes in the level and distribution patterns of sulphur oxide emissions.

Clean areas,such as those found in western North America are the most sensitive to visibility degradation. Usually, good visibility is valued most highly in natural settings such as parks and wilderness areas. Any area however, with normal viewing distances of a mile or more maybe affected by episodic regional haze carrying acid precursor substances.

Man-made Effects

Acid deposition, oxidants, gases and particulates collectively contribute to the accelerated degradation of materials. Many metallic construction materials are adversely affected by acid deposition through increased dissolution of protective surface oxides, or of the metal itself. Masonry materials containing carbonate, such as limestone or marble, are very susceptible to attack by acid deposition. Plastics, elastomers, and organic paints and coatings are degraded by oxidants, and by acid-catalyzed polymer decomposition. Physical, chemical or bacterial actions, resulting from available air pollutants, can contribute to deterioration and corrosion of these different types of materials.

Possibly the most difficult aspect, when viewed from an international perspective, will be the separation of the effects attributable to local emissions of gas and aerosols from those associated with transboundary flow.

Loading/Effects Relationship

A number of different approaches have been examined to assist in the task of deriving relationships between parameters of acid loading and system response. These models are all under active development, and in the aquatic sector they have advanced to the point where a preliminary application is possible, although it is important to stress that full validation remains to be achieved.

One model (Dickson), based on Scandinavian data, indicates that annual sulphate loadings of less than 15 to 17 kg/ha would be unlikely to degrade "moderately sensitive" lakes. The most sensitive lakes and streams are likely to be on the borderline of potential effects at an annual sulphate loading rate greater than 9 to 12 kg/ha.

A second model (Henriksen), also based on Scandinavian data, shows that precipitation pH of 4.5, and lakewater SO_4^{2-} concentration of 60 μeq/l, are the maximum tolerable for lake waters with 50 μeq Ca/l or more. This in-lake concentration of sulphate converts to a precipitation sulphate concentration of about 40 μeq/l The predicted reduction in precipitation sulphate concentrations to 40 μeq/l in heavily loaded areas is needed to improve the pH from about 4.2 to about 4.5 in order to protect moderately sensitive lakes. Highly sensitive lakes and streams may be protected at predicted precipitation levels of sulphate of 21 μeq/l, which should result in a pH of about 4.8 units.

A third model (Loucks et al), based on North American data, combines the physiological sensitivity of early life stages of fish to acute effects of H^+ and Al^{3+} with data on pH during flushing event (snowmelt or heavy rain). These data show that a pH depression (ΔpH) of 0.7 to 1.0 which will cause a response of substantial physiological significance. Given this dose/response relationship, a loading threshold may be defined as the episodic sulphate loading which, when subjected to a defined flushing event leads to the minimal biologically significant short-term H^+ and Al^{3+} exposure. This model suggests that a sulphate loading of 5 to 7 kg/ha/yr produces a critical surface water response (ΔpH in the range of 0.7 to 1.0) for streams in sensitive areas: a loading threshold of 7 kg SO_4^{2-}/ha/yr converts to about 21 μeq SO_4^{2-}/l (assuming 70 cm/yr precipitation).

None of the predictions of these models are yet viewed as acceptable targets. However, validation of these predictions is likely to produce numbers which fall within the range given by present information.

A number of approaches to mapping terrestrial sensitivity to acid precipitation have been undertaken in the U.S. and Canada. Recent discussions however, have indicated that the assessment of terrestrial sensitivity must consider, and distinguish between, those aspects of the terrestrial ecosystem which have an effect on forest and agricultural productivity, on the one hand, and aquatic sensitivity, on the other. Further refinement and mapping of the different criteria will be undertaken in Phase II.
In the man-made structure area, several approaches to modelling dose response relationships have been developed, using materials of known composition. However, interpolation of results from test conditions is difficult, largely because of a lack of environmental and meteorological data at the test sites.

SECTION 2

INTRODUCTION

PURPOSE AND SCOPE OF THIS REPORT

This document is the Phase I, January, 1981, interim report of the Canada/United States Impact Assessment Work Group. A major purpose of this report is to provide a description of the state of knowledge concerning the impacts of transboundary air pollution on each of four impacted areas: aquatic systems, terrestrial systems, man-made structures, and human health and visibility. The activities of the Work Group are being carried out through four subgroups, each addressing an impact area.

In providing a summary of the state of the knowledge, the report first provides a framework for understanding the transboundary air pollution problem. Then, for each of the four impact areas, it describes the principal, documented, physical and biological effects of long-range transport of pollutants - with emphasis on acid rain; discusses methods of defining sensitive areas; describes effects of atmospheric loadings with respect to time; attempts to establish targets for reduction of loadings - especially of acid rain; and lists research needs to further the scientific understanding of the problem and to outline a plan to monitor the effectiveness of abatement programs, to be established by the final agreement.

The ultimate product of the Impact Assessment Work Group is intended to be a definition of the maximum loadings of pollutants that can be tolerated by defined sensitive areas without unacceptable deterioration of those areas. To the extent that scientific knowledge permits, this end product will be included in the January 1982 report. These maximum loadings are referred to in this report as 'sustainable loadings'.

In Canada and the United States there has been a growing public awareness of the need for a clean environment. It is now recognized that this is not only necessary for the maintenance of a high quality of life, but it is also within economic reality. Wastes are now being treated or eliminated at the source, with less dependance on dilution by receiving media. The two countries' joint concern for the total environment was first evidenced by the 1909 Boundary Waters Treaty between Canada and the United States of America, which called for each country to prevent "injury to health or property on the other side of the boundary", and the 1972, and subsequent 1978, Great Lakes Water Quality Agreement, which further called for extensive protection of the Great Lakes ecosystem.

Figures 1 and 2 show a schematic representation of how air pollutants, particularly oxides of sulphur and nitrogen, are transported and deposited, causing acidic precipitation or acid rain.

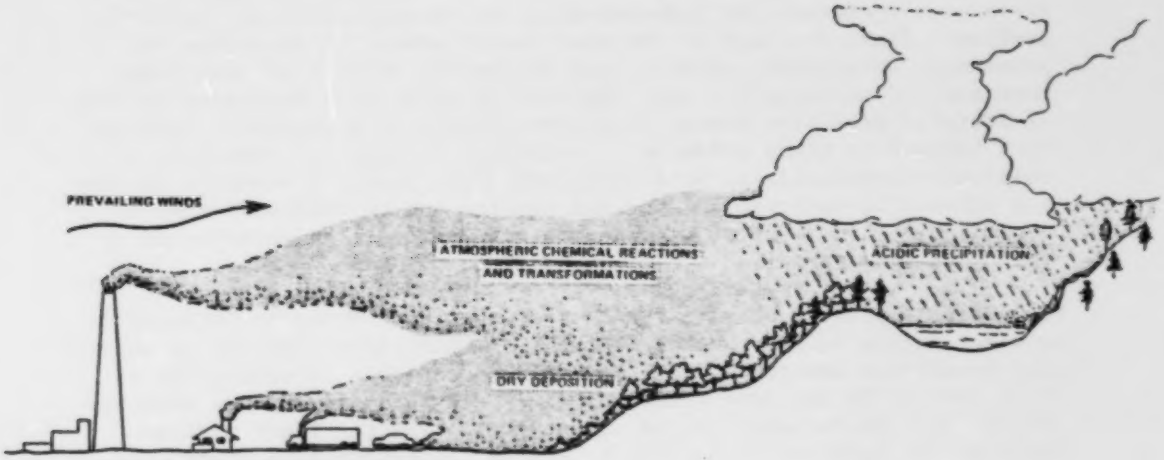
PREVAILING WINDS
ATMOSPHERIC CHEMICAL REACTIONS AND TRANSFORMATIONS
ACIDIC PRECIPITATION
DRY DEPOSITION

Figure 1. The transport and deposition of atmospheric pollutants, particularly oxides of sulphur and nitrogen, that contribute to acidic precipitation.

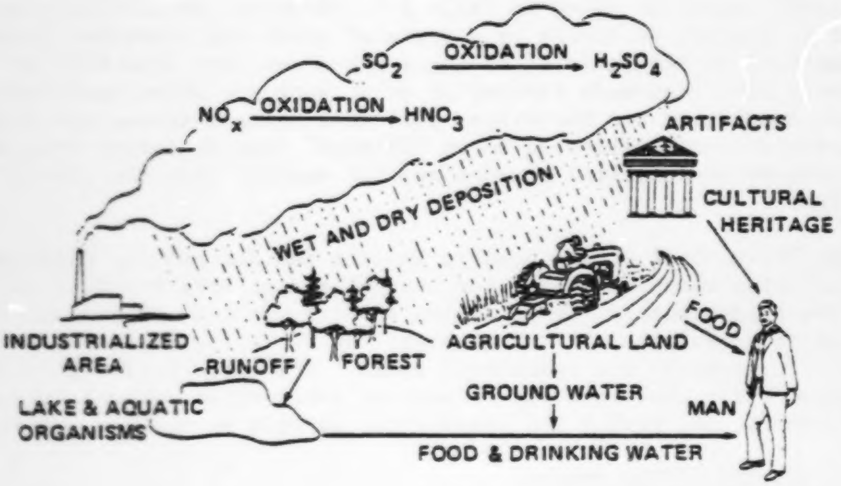
SO_2 OXIDATION H_2SO_4
NO_x OXIDATION HNO_3
ARTIFACTS
WET AND DRY DEPOSITION
CULTURAL HERITAGE
INDUSTRIALIZED AREA
RUNOFF
FOREST
AGRICULTURAL LAND
FOOD
GROUND WATER
LAKE & AQUATIC ORGANISMS
MAN
FOOD & DRINKING WATER

Figure 2. Schematic representation of some ways acidic precipitation affects the environment and man.

OVERVIEW OF THE NATURE OF TRANSBOUNDARY AIR POLLUTION PROBLEM

Although all pollutants eventually impact on the ecosystem, not all air pollutants generated by various sources cross international, state, or provincial boundaries. The main pollutants, which are, or have the potential to be harmful, are oxides of sulphur, oxides of nitrogen, particulates, oxidants and acid precipitation.

With sulphur dioxide as a notable exception, the natural sources of many gases far exceed the anthropogenic (man-made) sources, at least on a global basis, as shown in Table 2-1. However, deposition processes tend to operate partially on a regional scale and therefore observed background concentrations for these gases can vary from high to extremely low. Man-made sources of pollutants are often centered near urban complexes, and therefore, pollutant concentrations and related deposition can be elevated in an "airshed" that is larger than most watersheds or political boundaries, but smaller than the global circulation.

Pages 3-1 to 3-17 of the Aquatic Impacts Section provide additional information which is useful for the purpose of understanding the nature of the transboundary air pollution effects problem. These pages describe the complexity of the problem; how its effects are measured; and how it relates to the hydrologic cycle. The descriptions provide a framework for understanding effects on terrestrial systems, man-made structures, and health and visibility, as well as aquatic systems.

APPROACH FOR FUTURE PHASES

The ultimate success of the Impact Assessment Work Group in meeting its charges is dependent on the development of scientific information. Direct or indirect dose/response relationships can commonly be measured experimentally in the field or in the laboratory, but the slowness of many of the effects considered here requires long-term observation not yet available, or even initiated in many cases. The Work Group will continue to follow scientific developments closely for incorporation in future reports.

In some sensitive areas in the two countries, changes (responses) have been noted, but no information on exposure to pollutants (dose) is available. In such cases, in the absence of more information, the dose must be calculated using atmospheric transport and deposition models. The Impact Assessment Work Group not only provides input (sustainable loadings) to the Atmospheric Modelling Work Group, but also requires input (a calculated dose) from that Work Group, in order to carry out its mission.

Specifically, the objectives of the May, 1981 Phase II report are to provide a refined spatial/geographic resolution to the transboundary air pollution problem; to determine various loadings/effects relationships for individual regions or zones identified as sensitive; and to

TABLE 2-1

SUMMARY OF GLOBAL SOURCES, ANNUAL EMISSION, BACKGROUND CONCENTRATION, MAJOR SINKS, AND RESIDENCE TIME OF ATMOSPHERIC GASEOUS POLLUTANTS

Pollutant	Major Source		Estimated Emission kg/yr			Major Identified Sinks	Residence Time
	Anthropogenic	Natural	Anthropogenic	Natural	Concentration $\mu g\ m^{-3}$		Days
SO_2	Combustion of coal and oil	Volcanoes	130×10^9	2×10^9	1-4	Scavenging: Chemical reactions; Soil and surface water absorption; Dry deposition	5 (average)
	(North America)		16×10^9	0.8×10^9			
H_2S	Chemical processes: Sewage treatment	Volcanoes; Biological decay	3×10^9	100×10^9	0.3	Oxidation to SO_2	
N_2O	None	Biological decay	None	590×10^9	460-490	Photodissociation in stratopheria; Surface water & soil absorption	3,600
NO	Combustion	Bacterial action in soil; Photodissociation of N_2O and NO_2	53×10^9	768×10^9	0.3-2.5	Oxidation to NO_2	1-30
NO_2	Combustion	Bacterial action to soil;Oxidation to NO			2-2.5	Photochemical reactions; Oxidation to nitrate; Scavenging	1-30
NH_3	Coal burning fertilizer; Waste treatment	Biological decay	1×10^9	170×10^9		Reaction with SO_2 Oxidation to nitrate scavenging	
CO	Auto exhaust and other combustion processes	Oxidation of methane;photodissociation of CO_2;Forest Fires; Oceans	360×10^9	3000×10^9	100	Soil absorption ; Chemical oxidation	36
O_3	None	Tropospheric reactions and transport from stratospheria	None	(?)	20-60	Photochemical reactions; Absorption by land surfaces (Soil and Vegetation; Surface Water)	110
Non-reactive hydrocarbons	Auto exhaust ; Combustion of oil	Biological processes in swamps	70×10^9	300×10^9	CH I 1000 non-CH_4<1	Biological action	
Reactive hydrocarbons	Auto exhaust ; Combustion of oil	Biological processes in forests	27×10^9	175×10^9	<1	Photochemical oxidation	

From: Galloway and Whelpdale, 1980
Junge, 1972
Rasmussan and Sapal, 1975
Spadding, 1972

identify serious gaps in the knowledge base which require further attention.

The January, 1982 Phase III report will attempt to provide a definitive impact assessment of transboundary air pollution.

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Junge, C. 1972. Quant. J. Royal Meteorol. Soc. 98: 711-729.

Rasmussan, K.H., M. Taheri and R.L. Kabel. 1975. Water, Air, Soil, Pollution 4:33-64.

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SECTION 3

AQUATIC IMPACTS

INTRODUCTION

World attention was first drawn to the problem of transboundary pollutants, and their deposition on surface waters, in 1972, when Sweden reported the so-called "acid rain" phenomenon. From these Scandinavian studies, scientists in many other nations became increasingly aware not only of the failure of atmospheric dilution to solve waste problems, but also of the far-reaching effects on "receiving" aquatic ecosystems caused by the transport and deposition of pollutants. Since 1972, the acid deposition phenomenon has become recognized in North America, as detailed in many articles by both Canadian and U.S. scientists. North America today contains hundreds of atmospheric sources of sulphur and nitrogen oxides, all dependent on atmospheric dilution to resolve the gaseous residuals problem.

This Aquatic Impacts assessment is structured to deal with three major questions about aquatic impacts of long-range pollutant transport and deposition in North America.

1. How extensive is the chemical alteration of the hydrologic cycle due to pollutant deposition?
2. How extensive is the alteration of biota in aquatic ecosystems as a result of acid-induced chemical alteration?
3. What is the acid loading tolerance, or threshold, for watersheds of varying sensitivity?

This section uses several approaches to these questions. First, emphasis is placed on identifying and substantiating all effects possibly related to transboundary air pollution. This has required some consideration of the complexity of hydrologic systems as well as of the complexity and the extent of aquatic resources which are at risk. Included are detailed documentations of impacted aquatic environments, both chemical and biotic components, and definition of the time trends for observed effects on these components.

Secondly, this section considers the significance of the episodic nature of atmospheric pollutant loading, and pollutant flushing processes, such as snowmelt, as well as the seasonal character of the receiving environments, such as periods of spawning. Thus, these sections relate pollutant loading levels to the observed extremes in chemical and biological effects.

Finally, this section focuses on the aquatic areas and populations which are sensitive to acidic deposition, believed to result from transboundary air pollution. It is, therefore, necessary to define an acid-loading tolerance and to list aquatic resources at risk from higher loading levels; to identifying the geographic dimensions of sensitive areas; and to discuss recovery possibilities for aquatic systems showing apparent damage.

PROBLEM COMPLEXITY AND APPROACHES TO MEASURING AQUATIC IMPACTS

THE EXTENT OF RESOURCES AT RISK AND POTENTIAL FOR LARGE-SCALE EFFECTS

Acid deposition is currently being observed in most of eastern North America (Figure 3). Within this half-continent are large areas in which the surficial soil material and bedrock types have little ability to neutralize acids (buffering capacity), and which are identified as "potentially sensitive". These areas include some of the most unique, unspoiled and biologically productive environments on the continent. There are probably hundreds of thousand of lakes involved. Water covers about 8% of the surface area and plays a major role in the food chain of fish and wildlife in the region. The resultant effects on watersheds and aquatic resources are most strongly expressed in the areas where elevated inputs of acid combine with low natural buffering of soils and water to reduce the pH of surface water, leading to the extinction of fish populations. An important question, to be explored further in this report and in future studies, is whether the responses observed to date represent a time trend, thus suggesting that many more lakes will be affected in the future, or an equilibrium of inputs and weathering, thus suggesting little increase in the extent of damage, even if current acid loadings continue.

Recent increases in combustion emissions in the midwest, related changes in atmospheric pollutant deposition in the northern Great Lakes region, and the recent record of damage to resources in sensitive areas, are causes for concern in Canada, New England, the midwest states and mountainous regions of the west.

Over most of this area, acid rain, sulphate particulates, and oxidants occur together. In addition, there are local exposures to sulphur dioxide, nitrogen oxides and fluorides, with biological uptake and subsequent cycling of these elements. The acidic substances appear directly or indirectly, to cause most of the effects observed on aquatic lifeforms.

The potential is high for widespread environmental degradation, from acid rain and other pollutant deposition, because hydrogen ion concentration (acid, H^+) in the aquatic environment is a critical factor controlling most chemical reactions. Environmental processes, such as solubilization, corrosion, and mobilization of minerals and metals, are speeded up by increasing the acid concentrations in soils and water. Soil weathering and nutrient balances are altered by changes in the acidity of soilwater. Household water supplies from shallow wells, or

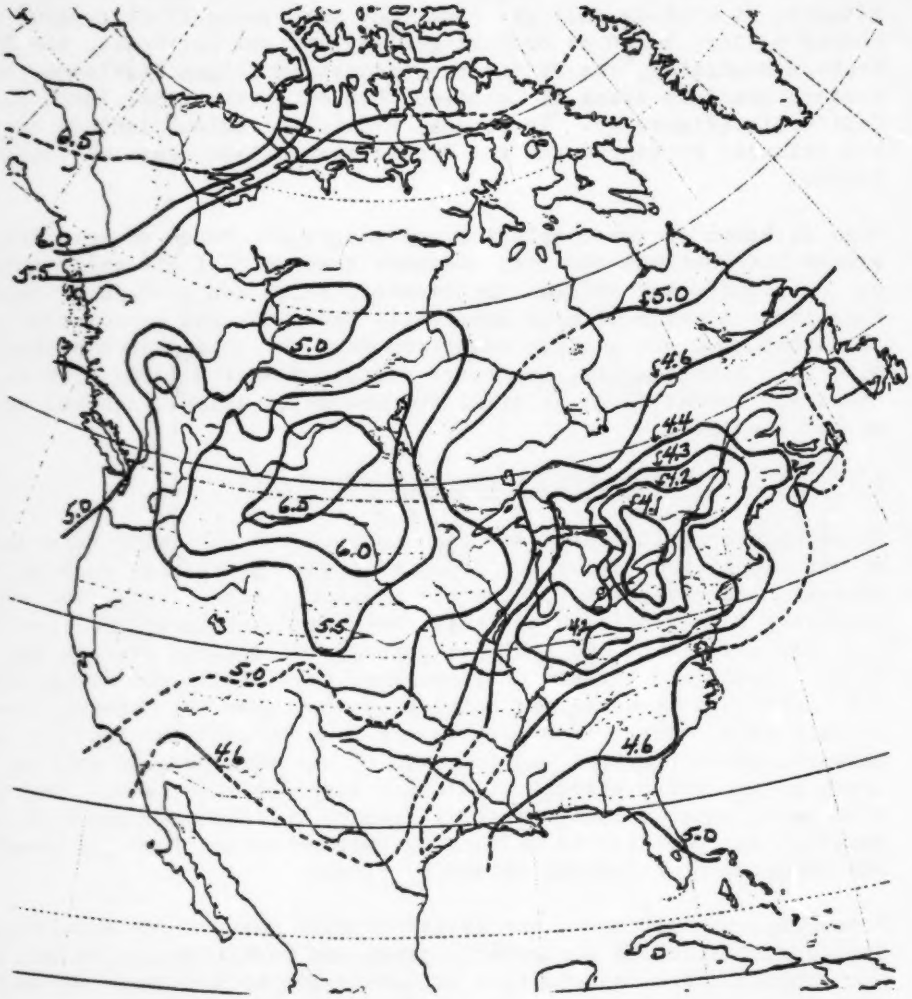
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Figure 3. Weighted mean pH of precipitation, annual average 1979 (Gibson, 1981).

acidic surface waters, in turn, can be modified by the further mobilization of metals from pipes. Metal culverts at stream crossings are especially susceptible to corrosion from mild acidity.

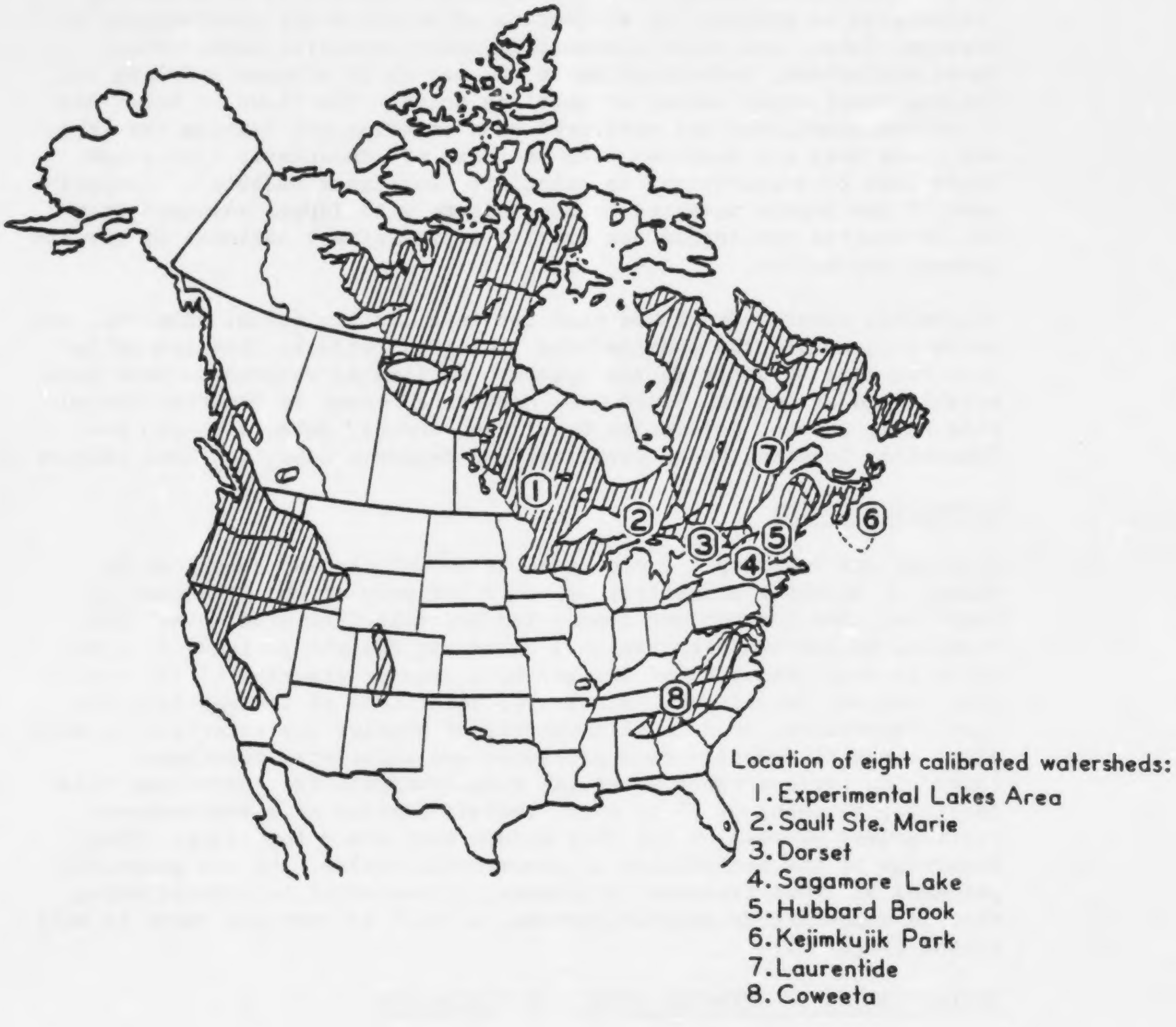
Despite the universal nature of these response processes, the potential susceptibility of watersheds to environmental damage from acid rain is quite different from one region to another due to differences in climate, as well as geology. The four most susceptible regions in the United States, based on bedrock geology are the Northeast, the Appalachian Mountains, the Minnesota-Wisconsin-Michigan highlands, and the western mountain areas of Colorado, Oregon, Washington, Idaho and California (Figure 4). In Canada, sensitive regions include parts of the Atlantic Provinces and the Precambrian shield areas of Ontario and Quebec.

What is known of the complexity and geographic range of acid rain-ecosystem interactions and long distance transport of air pollutants may pose a significant dilemma for federal, state and provincial regulatory agencies. Aquatic life is apparently being damaged by regional air emissions, but air quality standards were not designed to protect water quality. Nevertheless, important resources over a large part of the continent appear to be at risk, and new multinational control approaches may be required.

ACID DEPOSITION AND EFFECTS MEASUREMENT METHODS

Deposition of pollutants from the atmosphere occurs with rain and snow as wet deposition, or as dry deposition when particles, such as sulphate aerosols and gaseous SO_2, directly contact plants, soils, and water. Measuring the deposition of these three kinds of materials, in such a way that the direct and indirect pathways to aquatic systems are understood, requires a variety of approaches. Rainfall (wet deposition) is the easiest to measure, and samples can be taken for chemical analysis of each rain event. Snow samples are more difficult to collect and measure, since the size and location of the samplers, as well as wind speed at the site, strongly influence sampling efficiency. Dry deposition measurement techniques still require refinement because of inherent physical difficulties in collecting dust particles, and the complexity and importance of gaseous uptake by plants.

Presently, no instrument can satisfactorily measure dry deposition. The concentration of atmospheric gases and particles can be monitored, but sophisticated calculations of likely deposition rates on surfaces must be made. Differing amounts of forest and plant cover, water surface area, wind speed, etc., combine to lend uncertainty to gaseous deposition estimates. Therefore, while knowledge of the total loadings of atmospheric pollutants is important in understanding impacts on soils and water, exact measurement of the loadings is difficult.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Location of eight calibrated watersheds:
1. Experimental Lakes Area
2. Sault Ste. Marie
3. Dorset
4. Sagamore Lake
5. Hubbard Brook
6. Kejimkujik Park
7. Laurentide
8. Coweeta

Figure 4. Regions of North America containing lakes that are sensitive to acidification by acid precipitation, based on bedrock geology, showing where calibrated watershed studies on sensitive areas are in progress. (modified from Galloway and Cowling, 1978).

Lakes, rivers, and watersheds are the ultimate "collectors" of atmospheric pollution. Thus, one research approach has been to operate lakes and watersheds as large-scale, "calibrated" collectors, since the surface environment experiences a total loading, due to a combination of all deposition processes. This approach has led to establishing "calibrated watersheds" as monitoring sites which are combinations of streams, lakes, and plant communities under intensive measurement. In these watersheds, hydrologic weirs are set up in streams entering and leaving small study lakes, or settling pools. The flows of water and dissolved substances are monitored upon entering and leaving the lake, and these data are combined with measures of atmospheric inputs and water loss by evaporation, to calculate "substance budgets". Comparisons of the inputs measured by the budgets with inputs measured from wet deposition monitoring can provide a preliminary estimate of dry and gaseous deposition.

Calibrated watersheds can be used for detailed biological sampling, and serve to quantify the chemical and biological effects that air pollution can have on water in the system. Calibrated watersheds have been established at Kenora, Sault Ste. Marie and Dorset in Ontario; Laurentide Park, Quebec; Kejimkujik Park, Nova Scotia; Hubbard Brook, New Hampshire; Coweeta, North Carolina; and Sagamore Lake, New York (Figure 4).

HYDROLOGIC CYCLES

Although the hydrologic cycle seems to be well-known, questions do emerge as to the availability of water for many of the acid-forming reactions, and for the wet deposition and soil flux processes. For example, in low-humidity regions, or during drought periods, long-distance gaseous transport of SO_2 may be a greater fraction of the deposition than wet deposition. Similarly, conditions of low rainfall and high evaporation, or drought intervals of similar characteristics, will alter the soil solution flux processes and associated reactions. Indeed, in regions where potential evapotranspiration approaches total rainfall, flushing of H^+ or SO_4^{2-} becomes limited to a short-season (springtime) process or one that occurs only every few years. Thus, knowledge of the periodicity of atmospheric cycles, and the geographic patterns of these transport processes, is essential to understanding what is happening to aquatic systems, as well as when and where it will happen (Figure 5).

DOCUMENTATION OF IMPACTED AQUATIC ENVIRONMENTS

Precipitation Patterns and Hydrologic Cycle in Relation to Transboundary Pollutants

Acid precipitation is influenced by patterns of large-scale atmospheric behaviour as air masses circulate over North America. Areas of high precipitation, downwind from emission sources, receive greater acid

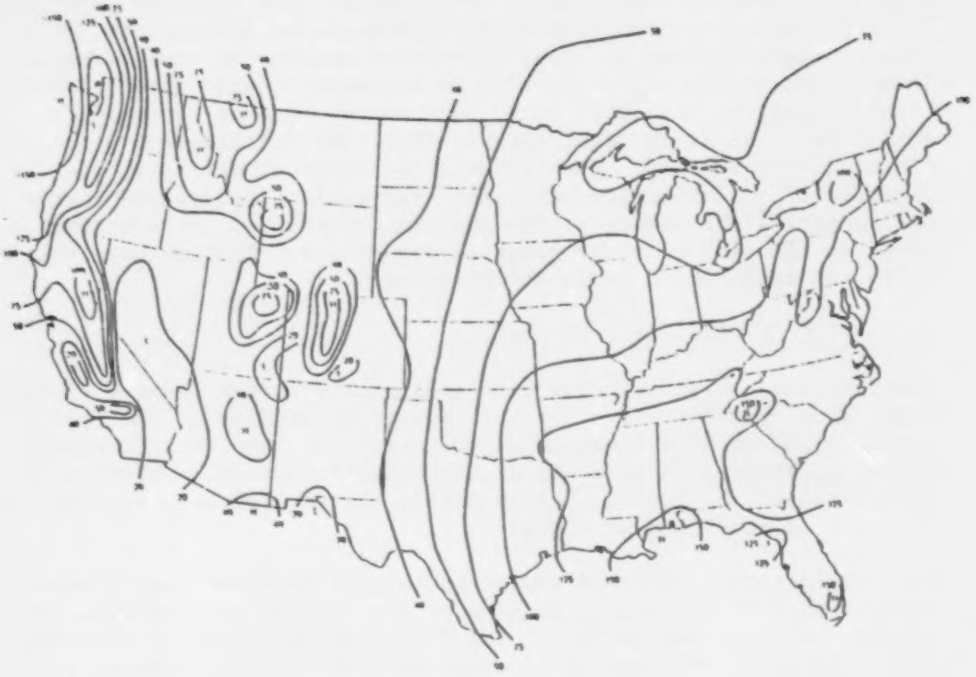

Figure 5. Approximate mean annual precipitation (cm) in the United States (based on "National Atlas" and "Climates of North America").

loadings. This pattern, for example, is observed in the mountainous areas of the northeastern United States where the higher elevations of New York and the Appalachian States receive very acidic rainfall and abundant precipitation (Figures 5 and 6).

Acid rain also appears to be deposited along major storm tracks, even when considered on a pH-weighted annual average. Isopleths of H^+ deposition for 1976-79 (Figure 6) tend to approximate storm track patterns which originate in eastern Texas, and continue across the Ohio River Basin into eastern Canada and the northeastern United States.

The seasonal quantity and quality of precipitation are important for determining the potential for acid rain impacts on the environment. Acid pollutants accumulating in the snowpack have a higher potential for causing deleterious effects on organisms and habitats in areas with higher snowfall, than in areas with lower amounts of snow accumulation. This is due to the rapid flushing of accumulated acid during snowmelt. Large storms, on the other hand, tend not to have as low a pH for the entire rainfall as do light rains. Thus, the distribution of precipitation during the year, the temporal behaviour of rainfall, and the location of pollution sources within rainfall pathways, are linked to the potential for damage to the aquatic ecosystems. In addition, many areas in the east with the greatest annual precipitation have the least buffering capacity in soils and waterways.

ALTERATION OF PRECIPITATION QUALITY

Precipitation in equilibrium with atmospheric carbon dioxide would have a pH value of about 5.6. Partial results of studies of the present levels of chemical alteration of precipitation have been presented in Figure 6, showing large areas of North America which received acid precipitation in 1976-79. Areas within the 50 isopleth received about 50 times as much acid as normal.

All precipitation contains a wide variety of chemical constituents from sources such as sea spray, dust particles and the natural cycling of carbon, nitrogen and sulphur. The discharge of wastes to the atmosphere increases the amounts of compounds containing elements, such as nitrogen, carbon and sulphur, and adds to the variety of compounds, such as PCBs and heavy metals which are found in rainfall. The four ions of most importance to rainfall acidity are: hydrogen (H^+), ammonium (NH_4^+), nitrate (NO_3^-) and sulphate (SO_4^{2-}). Some of the nitrogen and sulphur containing pollutants are oxidized to nitric and sulphuric acids, so that the acid content of precipitation is mainly a secondary result of the primary emissions.

Table 3-1 lists the concentrations of these four major ions in bulk precipitation, and the total bulk deposition, calculated as the concentrations recorded in bulk precipitation samples, multiplied by the

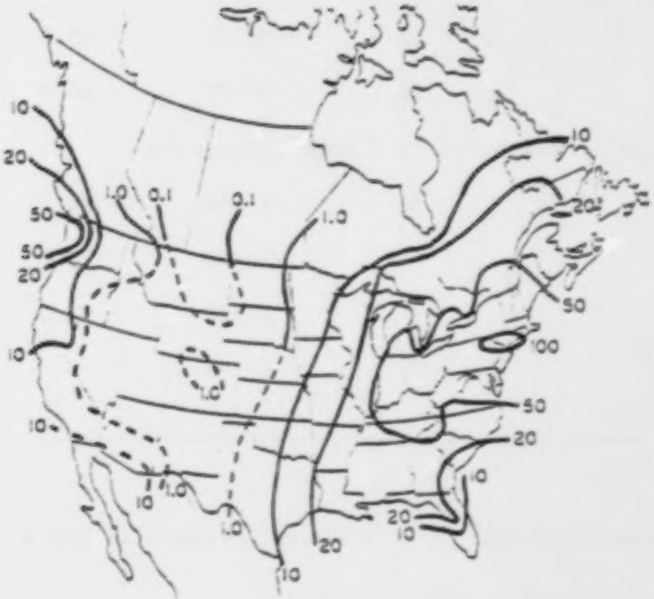
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Figure 6. Mean annual H^+ deposition in precipitation 1976-1979, kg/ha, estimated from weighted mean pH and mean annual precipitation (modified from Wisniewski and Keitz, 1980).

TABLE 3-1

CONCENTRATIONS IN BULK DEPOSITION AND TOTAL BULK DEPOSITION OF FOUR IONS AT FOUR CALIBRATED WATERSHED STUDIES. CONCENTRATIONS IN BULK DEPOSITION µeq/l.

	E.L.A.[1]	Dorset[2]	Hubbard Brook[3]	Kejimkujik* Park[4]
H^+	11	70-90	72.4	24
NH_4^+-N	21	34-36	12.2	4.4
NO_3^--N	18.5	36-41	23.7	12.4
SO_4^{2-}	30	77-89	60.3	33(28.5)
Deposition in meq/m^2/yr from bulk deposition				
H^+	10	55-58	96	34
NH_4^+-N	-	25-28	16	6
NO_3^--N	-	25-34	30.6	17
SO_4^{2-}	20.7	62-64	79	46(40)

* Wet deposition only, ( ) indicating excess sulphate.

From 1. Schindler et al., 1976
2. Scheider et al., 1979
3. Likens et al., 1977
4. Kerekes, 1980

total depth of rainfall, for sites in North America. Normal unpolluted precipitation has a hydrogen ion content of about 2.5 μeq/l (pH 5.6). It is evident that the most westerly study area, the Experimental Lakes Area, has an acid concentration of about four times normal, while Dorset and Hubbard Brook are about 30 times normal. Sulphate is the dominant anion. In the wet precipitation at Kejimkujik, the most easterly study area, the hydrogen ion concentration is about ten times normal, and sulphate is the second highest anion, surpassed by chloride (41 μeg/l), which is a reflection of the strong maritime influence on the precipitation in Nova Scotia.

Seasonal changes at given points have been studied. For example, the sulphate and nitrate concentrations in bulk deposition have been measured at Dorset, Ontario, since May, 1976. Winter data are for the snow collected by a winterized collector. Nitrate deposits do not vary greatly over the year, while sulphate varies seasonally with much higher depositions in the summer. The ratios of sulphate/ nitrate reflect the seasonal pattern. The data show that sulphur dominates, on the average, while, for short times in mid-winter, the two ions may be nearly equal. There have been single months such as December, 1976 when nitrate has dominated (W.R. Snyder, personal communication).

Additional information on both spatial (geographic) and temporal patterns in the chemical alteration of rainfall and snowfall will be presented in the Phase II report.

SURFACE WATER QUALITY

Nova Scotia and Newfoundland

Data from the mid 1950s for six rivers in Nova Scotia and one river in Newfoundland are compared with data for 1973 in Table 3-2. The results show decreases in pH and concurrent increases in excess SO_4^{2-} loads. The SO_4^{2-} being carried by these rivers is believed to have only two sources: long-distance transport of air pollutants, and sea salt. Atmospheric deposition of sulphate ions at two monitoring stations in Newfoundland was compared with the sulphate ions carried by the local rivers. The result was a general correlation between sulphate ion load in the rivers and the amounts from precipitation. Also shown was a geographic pattern of decreasing sulphate loadings to the east and north, which was consistent with an assumption of long-distance transport of pollutants from urban centres.

From considerations of the cation denudation rates of these rivers and their hydrologic regimes, Thompson and Bennett (1980) deduced that the mean pH of atmospheric precipitation in 1973 must have been 4.1 or 4.2 (Table 3-2). Stated another way, the H^+ load in southern Nova Scotia must have been about 110 meq/m^2, and about 130 meq/ m^2 to the Isle aux Morts River Basin. Figure 7 shows the rapidity with which these rivers responded to the changes in SO_4^{2-} loadings. The rivers were most acidic in 1973; the reason for the recovery after 1973 is not presently known.

TABLE 3-2

COMPARISON OF MEAN pH AND EXCESS SO_4^{2-} CONCENTRATIONS FROM THE MID 1950s to 1973, FOR SIX RIVERS IN NOVA SCOTIA AND ONE IN NEWFOUNDLAND

River	pH	Excess SO_4^{2-} meq m^{-2} yr^{-1}	Year
St. Mary's	6.20	42	1954-55
	5.16	60	1973
Roseway	4.66	30	1954-55
	4.28	128	1973
Tusket	5.16	51	1954-55
	4.38	101	1973
Mersey*	5.82	18	1954-55
	4.78	65	1973
Medway	5.67	29	1954-55
	4.88	78	1973
La Have	5.94	34	1954-55
	5.20	80	1973
Rocky River, Newfoundland	6.15	27	1955-56
	5.3	101	1973

* Discharge data incomplete 1954-55

From: Thompson et al., 1980.

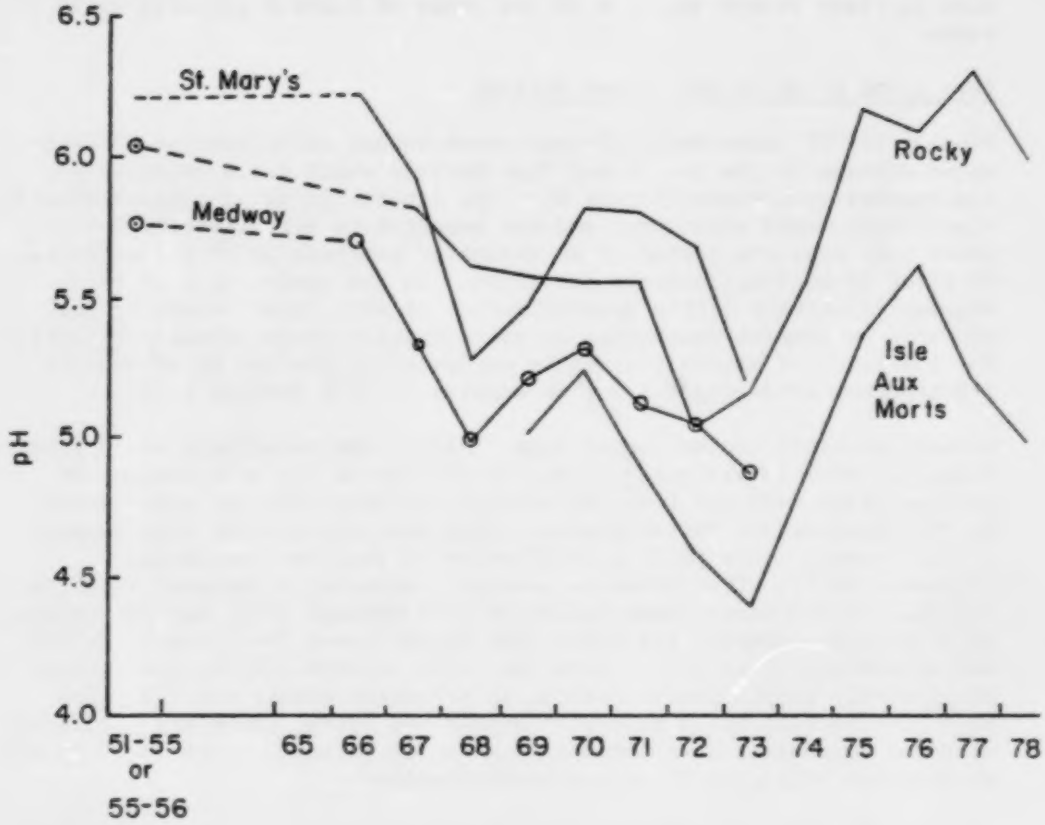

Figure 7. Time trend of pH for three rivers in Nova Scotia (Thompson et al., 1980).

Rates of Acidification in Salmon Rivers in Nova Scotia

Results obtained by Watt (1980) show that, within Nova Scotia, the distribution of acid surface water is well correlated with geological substrata. Seasonal variation in the pH of the rivers is about 0.5 units, with the annual minimum occurring in mid-winter, and a maximum in late summer. Historical data indicate that the rate of acidification in these rivers has been of the order of 0.3-0.4 pH units in 20 years.

Time Trend of pH in New Jersey Streams

Johnson (1979) described a 17-year trend toward acidification of headwater streams in the New Jersey Pine Barrens which drain relatively undisturbed watersheds (Figure 8). The decline in pH is a statistically significant trend with time, and has amounted to approximately 0.4 units (pH) over the period — an estimated increase in H^+ concentration of about 50 microequivalents per litre. In the sandy soils of this region, relatively little neutralization of acid input occurs by ion exchange or mineral weathering as precipitation moves through the soil. The low level of neutralization is evidenced by the low pH of shallow groundwater, averaging 4.3 for 78 samples in 1978 through 1979.

Several possible causes, which might lead to the relatively rapid acidification, were investigated. One possibility is the acid content of precipitation over the last two decades, as described for other areas in the northeastern United States. Some precipitation pH data suggest a trend toward lower pH of precipitation in southern New Jersey (Johnson, 1979). Precipitation samples, collected at several sites in the Mullica and Cedar Creek basins in 1970 through 1972, had an average pH of 4.4, and samples collected near Oyster Creek for 7 months in 1972 had an average pH of 4.25. From May, 1978 to April, 1979, the average pH of weekly precipitation samples at McDonalds Branch was 3.9. The SO_4^{2-} concentrations in McDonalds Branch and Oyster Creek are consistent with the hypothesis of an atmospheric source of acid, since SO_4^{2-} is the major anion balancing H^+ in the precipitation.

pH and Alkalinity Changes in North Carolina

Measurements of 38 streams in western North Carolina reported by Hendrey et al. (1980), showed a decrease in pH and alkalinity in 80% of the streams surveyed between 1960-63 and June and July, 1979. The distributions of apparent pH and alkalinity changed substantially over the 15 to 19 years between samples (Figures 9 and 10). Mean hydrogen ion concentrations changed from pH 6.77 in the early 1960s, to pH 6.51, in 1979, - an 82% increase in hydrogen ion concentration. Mean alkalinity values have also declined significantly since the early 1960s, from 116 μeq/l (corrected for differences in methods), to 80 μeq/l in 1979, with 71% of the 1979 values being lower than the earlier (corrected) values. Additional data are needed to confirm these observations.

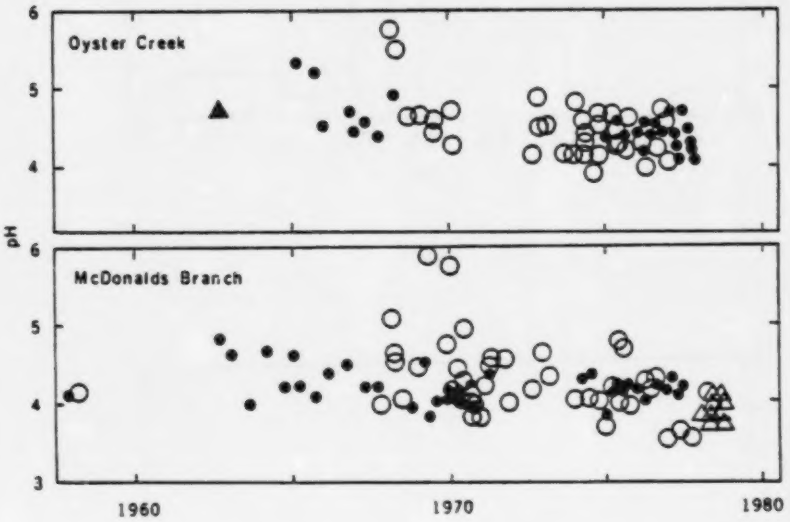

Figure 8. New Jersey stream pH, 1958-1979, Oyster Creek and McDonalds Branch. Closed circles represent samples in which anion and cation equivalents balanced and calculated and measured specific conductances were equal. Open circles are samples for which the chemical analyses were incomplete or for which discrepancies in anion and cation and conductivity balances could not be attributed to errors in pH. The closed triangle represents the average pH determined in a branch of Oyster Creek in a 1963 study. Open triangles are monthly means of pH data collected weekly from May 1978 to January 1979 during a University of Pennsylvania trace metal study (Johnson, 1979).

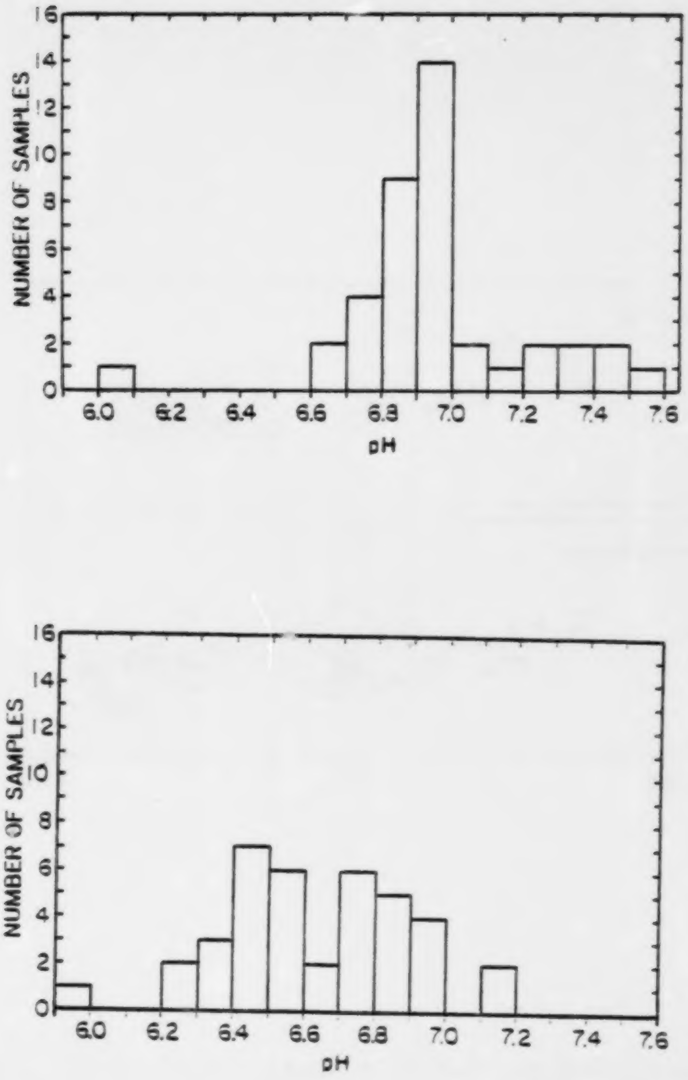

Figure 9. Distribution of pH of North Carolina streams June, July, August 1960-1963 (upper), compared with June, July 1979 (modified from Hendrey et al., 1980).

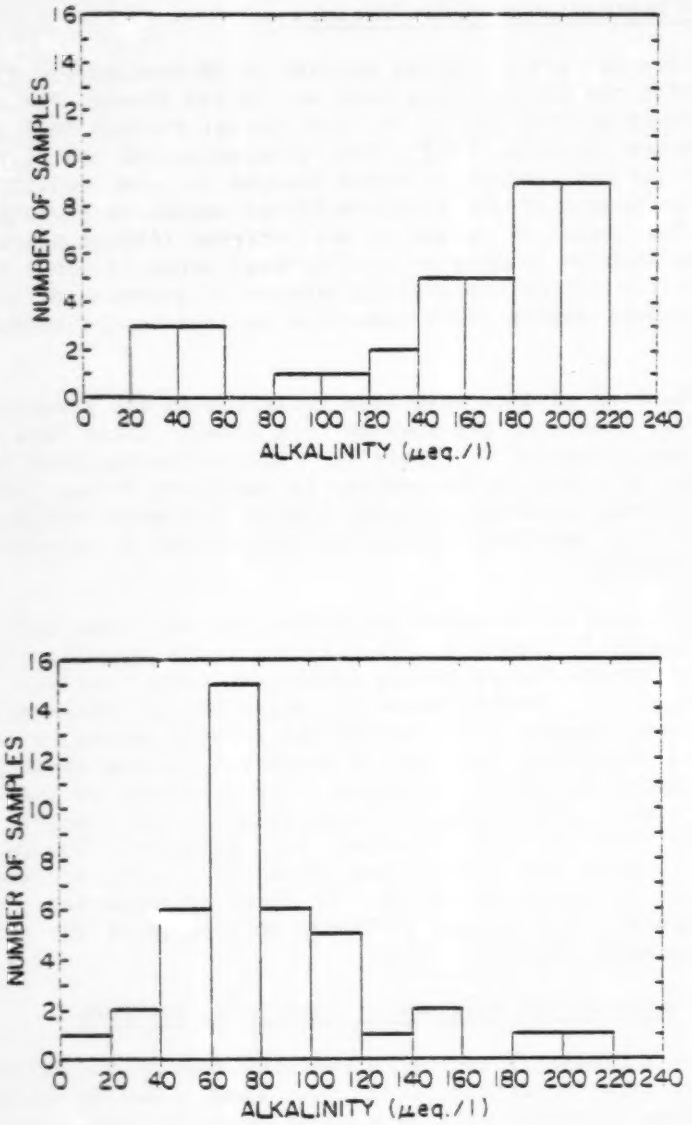

Figure 10. Distribution of alkalinity of North Carolina streams June, July, August 1960-1963 (upper), compared with June, July 1979 (modified from Hendrey et al., 1980).

Episodic pH Depression in West Virginia

Seasonally low pH, and a regular pattern of pH depression, have been documented for the Little Black Fork and in the Shavers Fork Rivers from monitoring carried out by the U.S. Forest Service in Monongahela National Forest (Dunshie, 1979). The tributaries and the river are poorly buffered and subject to rapid changes in water quality due to the strong influence of the poorly-buffered sandstone geology of the watershed. The lowest pH values in both streams (Little Black Fork is a control area with no logging or coal mining) normally occur during the winter and early spring, apparently because of snowpack melting. The highest pH occurs during low stream flow periods in the summer and fall.

Nearly 13 years of pH data have been collected at the Bowden Fish Hatchery river intake on the Shavers Fork River. These data summarized by season, are presented in Figure 11. The declining trend from a high in the summer to a low in the spring, is important for aquatic organisms, and has been measured in other lightly buffered streams. This pH trend occurs in stream and tributaries independent of watershed disturbance by mining.

The effect of rainfall on river pH is more apparent when individual events are examined. Graphic presentations, pairing daily river and precipitation events for pH during summer and winter periods, are shown in Figure 12. Daily precipitation accumulation and discharge are also shown. The data suggest that, during the growing season, a storm event, with a coinciding increase in discharge, lowers river pH below the natural non-storm daily variation. The magnitude of this downward shift is dependent upon rainfall characteristics (pH, amount, intensity, and areal distribution) and antecedent soil moisture. Downward shifts in river pH ranging from six to nine-tenths of a unit, occurred on July 11 and 26, and on August 15 and 25. On three of these days, at least 3.3 cm of rainfall fell within a 48-hour period; pH of the rainfall for these dates ranged from 3.7 to 4.2.

Lake pH in Waters of the Adirondack State Park, New York

Studies of lake chemistry in high-elevation lakes of the Adirondack region of New York (Schofield, 1976) have shown a marked decline in the pH of the lakes, compared with data of 40 years earlier (Figure 13). The decline in pH here has also been associated with failure of fish to reproduce, or at least to maintain populations in the youngest age classes. Of the 218 lakes measured in 1975, approximately 50% were significantly acidified in comparison to earlier observations. The positive correlation between increased elevation and reduced pH of ponds and lakes appears to reflect the combined influence of heavier precipitation at higher elevations, the smaller surface acreage and watershed size which characterizes most headwater ponds, and the prevalence of granitic bedrock and shallow soil deposits in the higher

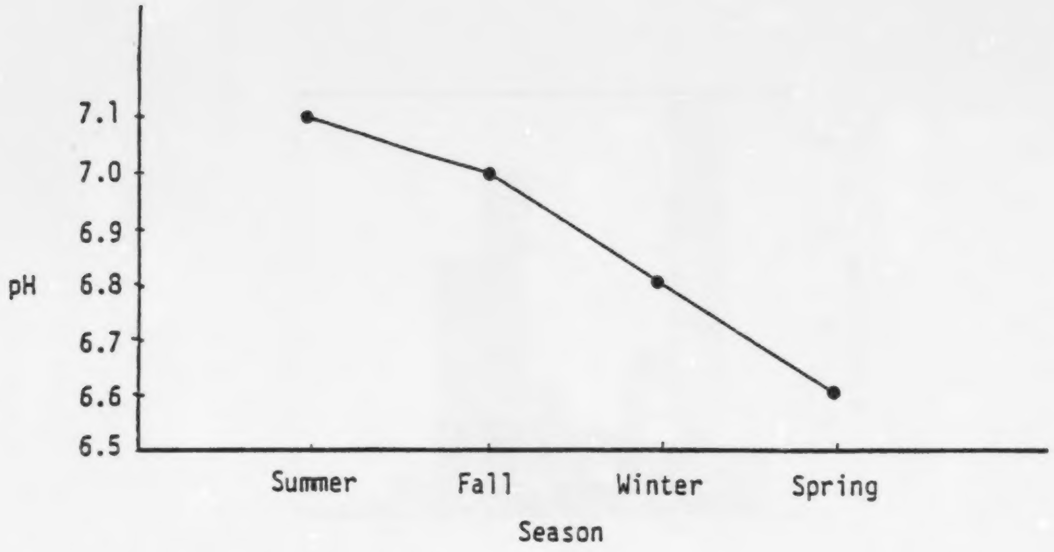

Figure 11. Seasonal summary of pH for Shavers Fork River at Bowden, West Virginia from 1966 to 1978 (Dunshie, 1979).

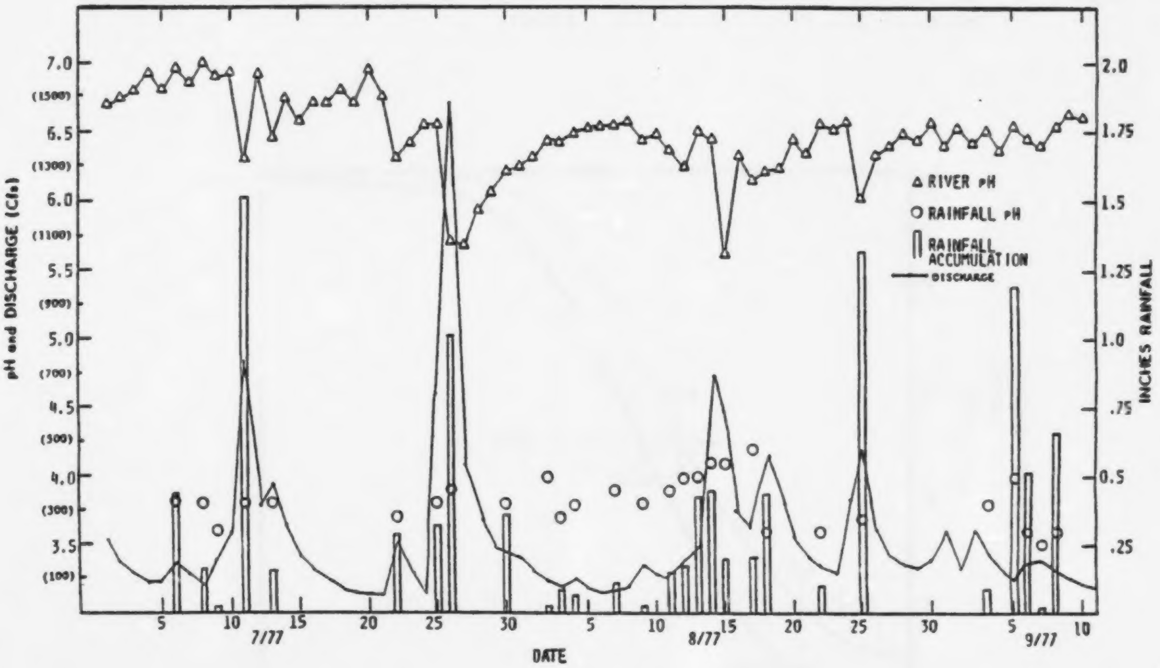

Figure 12. Mean daily pH for the Shavers Fork River at Bemis, West Virginia and precipitation event pH and accumulation at Arborvale, West Virginia (Dunshie, 1979).

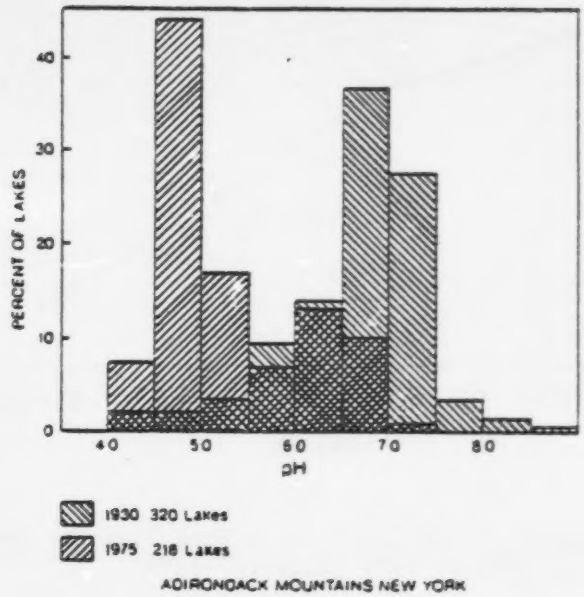

Figure 13. Comparison of lake pH, 1930 to 1975, for the Adirondack Mountains area of New York (Schofield, 1976).

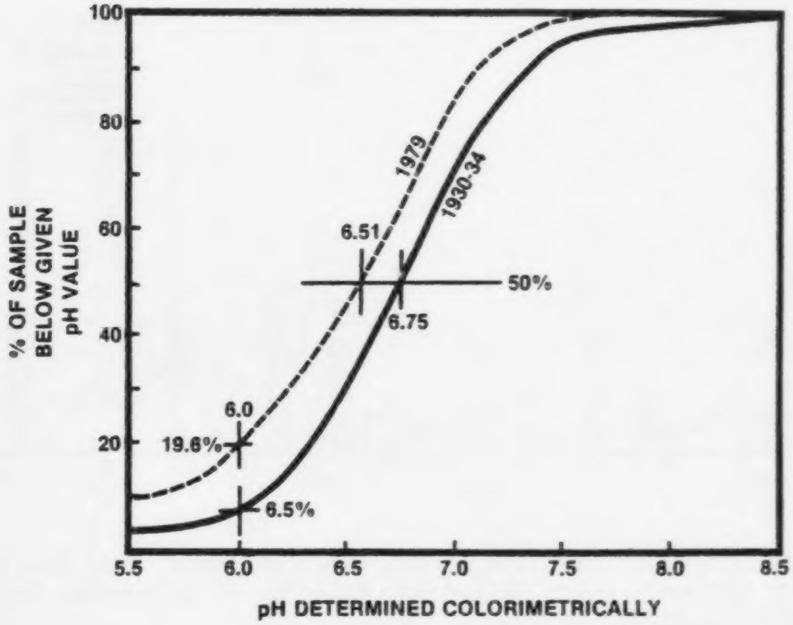

Figure 14. Cumulative comparison of historic and recent pH value for a set of 138 Adirondack Lakes, New York (Schofield, 1976).

areas. The most recent (1975 to 1979) New York State Department of Environmental Conservation surveys indicate that 25% of the lakes (comprising about 5% of the sampled waters) were at a "critical" pH level, below 5.0. Overall, 7.9% of the lakes in the Adirondacks were acidified from acid precipitation (228 lakes), totalling 3.9% of the water acreages.

Also, from these studies, there is evidence suggesting that decreases in pH have occurred over a wide range of lake pH values. A set of 138 lakes in the Adirondacks is summarized in Figure 14.

Alkalinity Time-trend at the Hinckley Reservoir, New York

The Hinckley Reservoir, a municipal water supply reservoir in New York state, receives the drainage of West Canada Creek, in the southwestern Adirondack Mountains. Water quality records have been maintained since 1924. Results for total hardness and alkalinity over the period 1924 to 1975 indicate a significant long-term decline, which may have begun before 1920. The significance of these results will be further evaluated during Phase II. Short-term upward and downward shifts in concentrations of alkalinity and hardness over the period, especially the increase in the early 1960's, appear to be due to drought conditions (C.L. Schofield, personal communication).

pH Trends of Lakes in Maine

Summer pH measurements are available for 1368 of the several thousand lakes in Maine, over the interval from the 1930s to the 1970s. The results show a decreased pH, on the average of from about 6.85 in 1937 to about 5.95 in 1974, an eight-fold increase in acidity. Roughly three-fourths of the decrease occurred between 1950 and 1960, correlating with the period in which the acidity of precipitation may have increased most rapidly (Haines, in press).

Seasonal pH Depression in Northern Minnesota

The effects of acid deposition on the Boundary Waters Canoe Area Wilderness (BWCAW) of northern Minnesota were assessed during a synoptic study of lakes and streams, before and after the snow season, 1978-79. Studies of several lakes and streams, during the snowmelt period, revealed relatively large decreases in pH and alkalinity in the surface waters. pH depressions of as much as 1 unit were noted (Figure 15). Changes in water quality occurred, concurrent with the spring melt and the release of accumulated materials (SO_4^{2-}, NO_3^-, H^+). In addition, there were contributions from watershed soils (Ca^{2+}) (Glass, 1980).

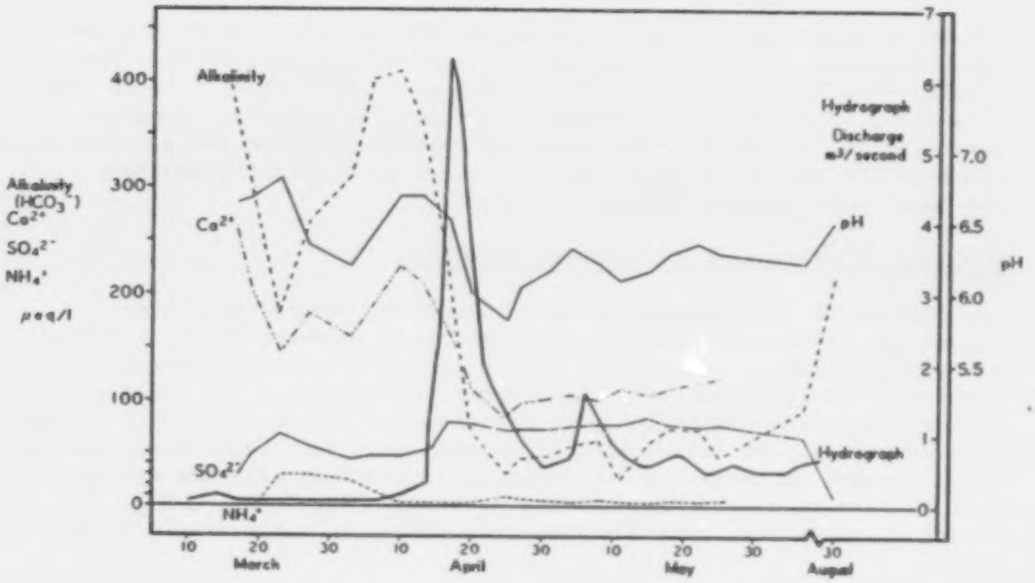

Figure 15. Stream water quality changes during the 1979 snow melt for Filson Creek near the BWCAW of northern Minnesota (Glass, 1980).

ELEMENT FLUXES AND GEOCHEMICAL ALTERATIONS OF WATERSHEDS

Ionic balances of watersheds have been used as a means of quantifying the net basin reactions resulting from acid precipitation. Several studies have been under way since the early 1960s. The earliest study, and the longest record (1963-1974), is the work at Hubbard Brook, summarized by Likens et al. (1977).

The bulk ionic composition of precipitation at the Hubbard Brook ecosystem is essentially characterized by acids, such as H_2SO_4, HN_3, and HCl. In contrast, water leaving the system is characterized mainly by neutral salts, composed of Ca^{++}, Mg^{++} and Na^+ balanced in solution by HCO_3^- and SO_4^{--} and to a lesser extent, by chloride and bicarbonate species. The chemical and biological reactions of hydrogen ion, nitrate, ammonium and sulphate are very important in driving displacement and weathering reactions, especially when considering the effects of acidic precipitation.

The Hydrogen Ion

The hydrogen ion driving the chemical weathering reaction is supplied from external and internal sources. The external source is the acid supplied in bulk precipitation (meteorological input); the internal source stems from various biologic and chemical processes occurring within the soil zone. The average external net annual input of hydrogen ion equivalent, observed at the Hubbard Brook watershed over the 1963-74 decade, was 865±33 eq/ha/yr (Likens et al., 1977). If this were the only source of H^+ ions at Hubbard Brook (and the ecosystem were in a steady state), one might expect this value for hydrogen fixation to be more or less balanced by the net rate at which ionic Ca, Mg, K, Na, and Al are leached from the system. In fact, there are more of these cations removed from the ecosystem each year than there are external hydrogen ions to replace them. The difference is statistically significant, and implies the action of internally generated H^+.

The amounts of hydrogen ion being deposited from acid precipitation, generally, are in the range of 50-100 $meq/m^2/yr$ for the most heavily loaded areas, corresponding to 25 and 50 kg/ha/yr of calcium carbonate. Limestone soils can neutralize this amount of acid for an indefinite time, resulting in only a slight increase in total runoff of salts. However, in the Precambrian areas, the amounts of salts and alkaline materials being leached are in the order of 10 to 100 $meq/m^2/yr$. In Precambrian areas, therefore, hydrogen ion loadings are of the same magnitude and appear likely to influence normal weathering processes and modify the quality of surface runoff. In most parts of the Precambrian Shield, hydrogen ions from rainfall are neutralized during most of the year. Retention or neutralization of hydrogen ions has been measured at 88, 94 and 98 percent, on an annual basis, at Experimental Lakes Area, Hubbard Brook and Dorset respectively (Schindler, 1976; Likens et al., 1977; Scheider et al., 1979).

Hydrogen ions deposited in snow tend to be stripped from snow crystals early in the spring snowmelt process. Thus, much of the total annual H^+ export from the watershed occurs during a brief period in the spring. The large volume of water, coupled with less opportunity for partial infiltration and interaction with soil, results in "shock level" concentrations of acid to streams and surface waters of lakes (Schofield, 1980).

Likens et al., (1979) summarize their results by noting that the internal sources of H^+ at Hubbard Brook enter as: (1) nitrogen compounds, particularly NH_4^+ inputs; (2) reduced carbon oxidized in the soil zone; (3) the production of organic acids, such as citric, tartaric, tannic, and oxalic acid, by biologic activity within the soil zone; and (4) small amounts of sulphide minerals in the bedrock, which are subject to oxidation, with the concomitant production of sulphuric acid.

Nitrate and Ammonium Ions

The atmospheric deposition of nitrate ion tends to range from 1/3 to 1/2 of the rate of sulphate deposition in eastern North America, to about 60% of acid fractions in rainfall in the western United States (Liljestrand and Morgan, 1978). The significance of the nitrogen component of acid precipitation is difficult to interpret with any broad generality, since it has more complex response processes than those of sulphate.

The molecular forms of nitrogen, deposited in acid rain, can result in either acidification or neutralization of surface waters. Nitrogen, as nitrate ions (NO_3^-), can be incorporated directly by vegetation, and the resulting reactions release hydroxyl ions (OH^-) into the environment (Figure 16). The hydroxyl ions can raise the pH of the soil and water, or neutralize the hydrogen ions of the nitric acid. Natural decomposition of nitrogenous plant materials also releases hydrogen ions, but net accumulation of plant tissue dominates in most ecosystems; hence, net production of neutralizing capacity from nitrate addition is usually dominant. This is particularly significant where forest harvest, rather than decomposition, removes plant materials.

Ammonium salts are deposited with the sulphate particulates, both dry and wet. Ammonium is a source of hydrogen ions (Figure 16) when the nitrogen is utilized by plants. This release of hydrogen ions can be a significant source of acidification in poorly buffered soils and surface waters. However, nitrogen is usually in short supply in terrestrial habitats, and is readily incorporated and retained by ecosystems (Reuss, 1976). The uptake and retention of nitrate and ammonium by forested watersheds is summarized in Table 3-3.

As with acid sulphates, nitric acid (nitrates) and ammonium salts can be stored in the snowpack of northeastern North America, and are

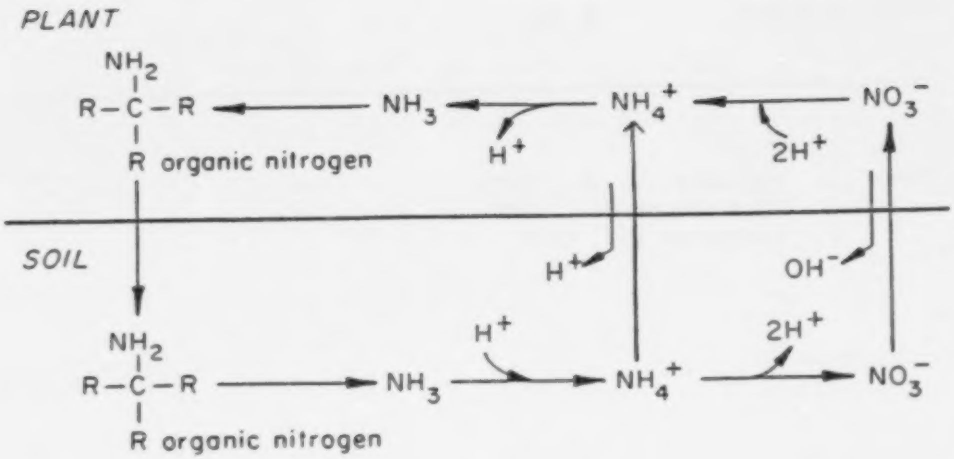
PLANT
SOIL
R organic nitrogen
R organic nitrogen
NH$_3$
NH$_4^+$
NO$_3^-$
H$^+$
2H$^+$
OH$^-$

Figure 16. Simplified nitrogen cycle showing chemical changes caused by plant and soil processes (modified from Reuss, 1976).

TABLE 3-3

THE UPTAKE OF NITRATE, AMMONIUM ION AND TOTAL NITROGEN BY FORESTED WATERSHEDS IN THREE CALIBRATED WATERSHED STUDIES

Substance	% Retention in the watershed on an annual basis E.L.A.[1.]	 Dorset[2.]	 Hubbard Brook[3.]
NO_3^-	-	75	83
NH_4^+	-	95	99
Total nitrogen	81-90	-	-

From: 1. Schindler et al., 1976
2. Scheider et al., 1979
3. Likens et al., 1977

released as acid components to aquatic habitats during spring snowmelt. During the growing season, however, both terrestrial and aquatic vegetation take up nitrates, and may, therefore, be partially responsible for the observed decreases in acidity in aquatic ecosystems. The fact that nitrate tends to be in greater quantity in precipitation than ammonium ions, and that both are largely taken up by vegetation, results in a net effect of production of alkalinity.

Sulphate

Sulphur, like nitrogen, is an essential plant nutrient, but it is usually in adequate supply for plant growth, simply through normal decomposition of plant tissues. Sulphate ions can be adsorbed in soils, or reduced mainly by bacterial action, which consumes acid, thus raising the pH of the soil-water environment. The sulphide form (S^{2-}) can be oxidized to sulfate, resulting in the production of hydrogen ions. Sulphate, then, can react in ways analogous to nitrogen, and its influence on acidification can also be analogous.

In spite of many possible reactions, much of the SO_4^{2-} deposited in acid precipitation is not retained in Precambrian Shield watersheds; thus, sulphate tends to be the anion balancing the transport of H^+ in surface water and shallow groundwater. The amount of SO_4^{2-} in runoff from the Shield areas is very close to the amount deposited. At the Experimental Lakes Area in Ontario, Schindler et al., (1976) found virtually 100% of the atmospheric SO_4^{2-} input in the runoff. Likens et al., (1977) found 67% of the total input in runoff at Hubbard Brook, New Hampshire, and Dillon et al., (1980) found 25% more SO_4^{2-} in runoff from four watersheds than was measured in the bulk deposition. This "excess" SO_4^{2-} may be due to unmeasured inputs by dry and gaseous deposition, but may be due to errors in the budget.

Ultimately, excess SO_4^{2-} can be leached through the poorly buffered soils of these regions, in association with cations released from exchange sites. Sulphur taken up by vegetation (or SO_2 absorbed by foliage) is subsequently reduced to the SO^{2-} state (primarily as amino acids) during decomposition, thus returning to an initial state of the sulphur cycle (Figure 17).

The results presented in the sections on nitrate and ammonium ions, and sulphate, have shown that most of the nitrogen added to the watershed is retained by plants in accreting ecosystems and, following a period of sulphate saturation in soils, most of the sulphur passes through to aquatic systems. Thus, it appears that control of sulphate deposition would be more effective in reducing the rate of acidification of surface waters than control of nitrogen inputs.

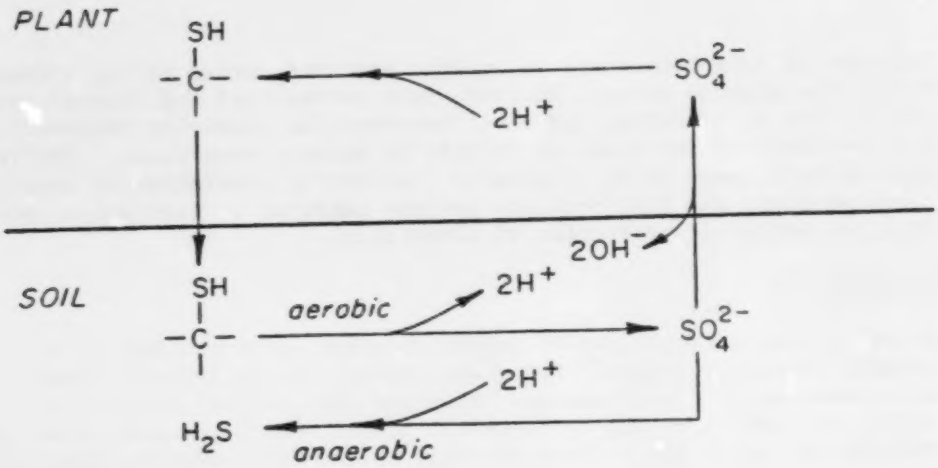
PLANT
SH
-C-
SO_4^{2-}
$2H^+$
$2OH^-$
SOIL
SH
-C-
aerobic
$2H^+$
SO_4^{2-}
$2H^+$
H_2S
anaerobic

Figure 17. Simplified sulphur cycle showing chemical changes caused by plant and soil processes (modified from Reuss, 1976).

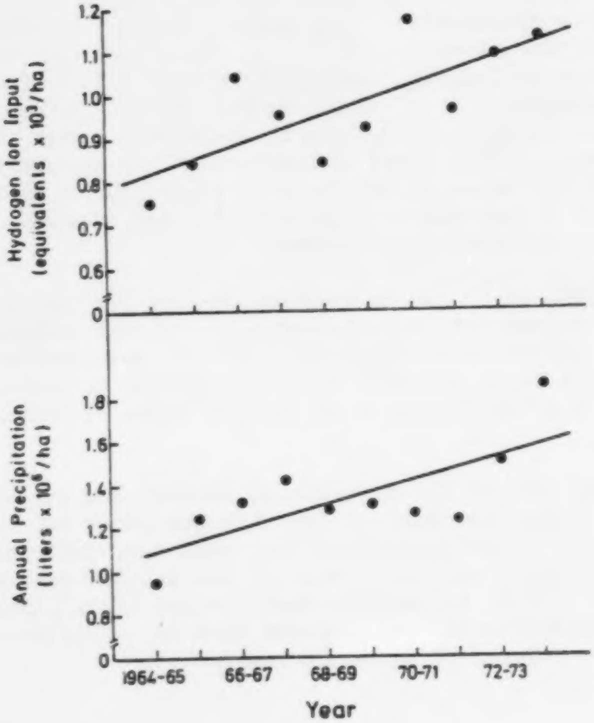

Figure 18. Annual hydrogen ion and precipitation input for the Hubbard Brook Experimental Forest, New York (Likens et al., 1976).

CATION AND ANION BUDGETS

Hubbard Brook, New Hampshire

Observed trends and completed annual ion budgets for 11 years at Hubbard Brook demonstrate the influence of atmospheric inputs on surface water quality.

Unusually high rates of H^+, NO_3^-, and SO_4^{2-} inputs were observed as early as 1964. The average annual weighted pH from 1964-1965 through 1973-1974 ranged between 4.03 and 4.21. The lowest value recorded for a storm at Hubbard Brook was pH 3.0 and the highest was 5.95. During the period 1969-1974 (the latter being the last year of the 1977 summary), no weekly precipitation exceeded a pH of 5.0. Figure 18 demonstrates that, although hydrogen ion concentrations are variable from year to year, the annual input of H^+ (concentration times volume) in precipitation increased by 1.4 times during the period 1964-1965 to 1973-1974. However, Likens et al., (1977) report no trend in H^+ concentration to be statistically significant. This increased input of hydrogen ion is in sharp contrast to the annual input of all other ions, which, except for nitrate, remained constant, or decreased. Concentrations for SO_4^{2-} and NH_4^+ vary from year to year, but show no statistically significant trends for the period. In contrast, annual weighted NO_3^- concentrations were about 2.3-fold greater in 1974 than they were in 1955-1956 or in 1964-1965.

The Hubbard Brook study site is an isolated headwater catchment, thus, the influx of chemicals is limited to precipitation and dry deposition, and the outflow to drainage waters. Theoretically, differences between annual input and output for a given chemical indicate whether that constituent is being accumulated within the ecosystem; is being lost from the system; or is simply passing through the system. Likens et al., (1977) therefore, were able to estimate, with some accuracy, the mean annual budgets for most of the major ions (Table 3-4). Over the long term, there is considerable variation; however, a net annual loss of calcium, magnesium, potassium, sodium, sulphate, aluminum, and dissolved silica, and a net annual gain of ammonium, hydrogen ion, and phosphate, have occurred from these undisturbed, accreting watershed ecosystems.

Overall, during 1964-1974, there was an annual net loss of total dissolved inorganic substances from the experimental watersheds, amounting to 75.8 kg/ha/yr. The average net output of dissolved inorganic substances minus dissolved silica (1963-1974), was 37.4 kg/ha/yr. The smallest annual net loss of dissolved inorganic substances (27.8 kg/ha, or 7.0 kg/ha) for total material, minus dissolved silica, occurred during 1964-1965, the driest year of the study. The largest net losses of dissolved inorganic substances occurred during the wettest year, 1973-1974 (139.7 kg/ha, or 986 cationic equivalents per hectare).

TABLE 3-4

ANNUAL BUDGETS OF BULK PRECIPITATION INPUTS AND STREAM-WATER OUTPUTS OF DISSOLVED SUBSTANCES FOR UNDISTURBED WATERSHEDS OF THE HUBBARD BROOK EXPERIMENT FOREST

(LIKENS et al, 1977)

Substance (kg/ha)	1963 to 1964	1964 to 1965	1965 to 1966	1966 to 1967	1967 to 1968	1968 to 1969	1969 to 1970	1970 to 1971	1971 to 1972	1972 to 1973	1973 to 1974	Total 1963-1974 kg/ha	Annual mean kg/ha
CALCIUM													
Input	3.0	2.8	2.7	2.7	2.8	1.6	2.3	1.5	1.2	1.2	2.0	23.8	2.2
Output	12.8	6.3	11.5	12.3	14.2	13.8	16.7	13.9	12.4	15.6	21.7	151.2	13.7
Net	-9.8	-3.5	-8.8	-9.6	-11.4	-12.2	-14.4	-12.4	-11.2	-14.4	-19.7	-127.4	-11.5
MAGNESIUM													
Input	0.7	1.1	0.7	0.5	0.7	0.3	0.5	0.5	0.4	0.5	0.4	6.3	0.6
Output	2.5	1.8	2.9	3.1	3.7	3.3	3.5	3.1	2.8	3.3	4.6	34.6	3.1
Net	-1.8	-0.7	-2.2	-2.6	-3.0	-3.0	-3.0	-2.6	-2.4	-2.8	-4.2	-28.3	-2.5
ALUMINUM													
Input	*	*	*	*	*	*	*	*	*	*	*	*	*
Output	1.6°	1.2	1.7	1.9	2.1	2.2	2.2	1.8°	1.7°	2.3°	3.2°	21.9	2.0
Net	-1.6	-1.2	-1.7	-1.9	-2.1	-2.2	-2.2	-1.8	-1.7	-2.3	-3.2	-21.9	-2.0
AMMONIUM													
Input	2.6°	2.1	2.6	2.4	3.2	3.1	2.7	3.9	2.8	2.5	3.7	31.6	2.9
Output	0.27°	0.27	0.92	0.45	0.24	0.16	0.51	0.23	0.05	0.18	0.42	3.7	0.34
Net	2.3	1.8	1.7	2.0	3.0	2.9	2.2	3.7	2.8	2.3	3.3	27.9	2.6
HYDROGEN													
Input	0.85°	0.76	0.85	1.05	0.96	0.85	0.93	1.18	0.97	1.08	1.14	10.62	0.96
Output	0.08°	0.06°	0.05	0.07	0.06	0.09	0.09	0.14	0.13	0.16	0.20	1.13	0.10
Net	0.77	0.70	0.80	0.98	0.90	0.76	0.84	1.04	0.84	0.92	0.94	9.49	0.86
SULPHATE													
Input	33.7°	30.0	41.6	42.0	46.7	31.2	29.3	34.6	33.0	43.4	52.8	418.3	38.0
Output	42.7°	30.8	47.8	52.5	58.5	53.3	48.1	51.1	46.8	64.0	84.7	580.3	52.8
Net	-9.0	-0.8	-6.2	-10.5	-11.8	-22.1	-18.8	-16.5	-13.8	-20.6	-31.9	-162.0	-14.8
NITRATE													
Input	12.8**	6.7	17.4	19.9	22.3	15.3	14.9	21.6	21.4	26.3	30.9	209.5	19.0
Output	6.7**	5.6	6.5	6.6	12.7	12.2	29.6	24.9	18.7	19.2	34.8	177.5	16.1
Net	6.1	1.1	10.9	13.3	9.6	3.1	-14.7	-3.3	2.7	7.1	-3.9	32.0	2.9
BICARBONATE* **													
Input	*	*	*	*	*	*	*	*	*	*	*	*	*
Output	6.2°	4.6°	6.2	9.4	9.6	7.0	6.0	7.1°	6.6°	9.0°	12.5°	84.2	7.7
Net	-6.2	-4.6	-6.2	-9.4	-9.6	-7.0	-6.0	-7.1	-6.6	-9.0	-12.5	-84.2	-7.7

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* Not measured, but trace quantities.

○ Calculated value based on weighted average concentration during years when chemical measurements were made and on amount of precipitation or streamflow during the specific year.

** Calculated from weighted concentration for 1964-1966 times precipitation for 1963-1964. Based on annual concentration of 0.50 mg/l (Juang and Johnson, 1967).

*** Watershed 4 only.

Likens et al., (1977) also note the complexity of the long-term cationic denudation in the Hubbard Brook ecosystem, due to accumulations of living and dead biomass. The net accretion of biomass should be viewed as representing a long-term sink for some of the nutrients supplied from the weathering reactions. The total amount of cations sequestered by this means is 722 eq/ha/yr. They conclude: (a) that cations stored within the biomass must be included in calculations of contemporary weathering; (b) that the rate of storage is a consequence of the ecosystem's current state of forest succession, and so changes with time; and (c) that the existence of the forest, and its state of development, must be included in geological estimates of weathering.

If this appraisal of the biological system at Hubbard Brook is correct, the flux of cationic nutrients being diverted into biomass accretion (772 eq/ha/yr) must be added to that actually removed from the system, in the form of dissolved load (1,267 eq/ha/yr) and particulate organic matter (10 eq/ha/yr). Therefore, their best estimation of cationic denudation (net loss from ecosystem plus long-term storage within the system) at Hubbard Brook is about 2,000 eq/ha/yr.

These long-term estimates of cationic denudation at Hubbard Brook allow estimation of the relative importance of external and internal sources of H^+ ions. The external supply rate is 1,000 eq/ha/yr and, by difference, the internal source becomes ~1,000 eq/ha/yr. This suggests that, under prevailing biological and chemical conditions (perhaps altered by changes in atmospheric precipitation), external and internal generation of H^+ ions play nearly equal roles in driving the weathering reactions.

Lake pH and Element Budgets in the Muskoka/Haliburton Area

Jeffries et al., (1979) compared pH values of a series of small streams in the vicinity of Dorset, Ontario, before and during spring runoff (Table 3-5). The pH of the lake outflows demonstrates that the surface waters, at least, of the entire lakes were acidified during this period of time. The lowest pH values observed, 4.1 to 5.1, are within a range capable of causing damage to aquatic life, particularly fish. As much as 76.6% of the measured yearly acid discharge from the streams ran off in April. Figure 19 shows a typical hydrograph and pH response for one of the streams during the snowmelt period. Scheider et al., (1978) further showed that the pH of streams was depressed for periods of as little as a few hours during times of heavy runoff, during the summer months (Figure 20).

Heavy Fall rains also cause depressed pH in runoff for days at a time. Scheider et al., (1978) observed as much as 25.8% of the total annual hydrogen ion runoff, from small watersheds, in October. The biological implications of these periodic pH depressions are just now being studied in detail.

TABLE 3-5

pH OF STREAMS IN MUSKOKA-HALIBURTON, ONTARIO, CANADA: STREAM pH IS GIVEN PRIOR TO SPRING RUNOFF (MID-MARCH 1978) AND AT MAXIMUM RUNOFF (MID-APRIL 1978)

Watershed	Stream	pH	
		Mid-March	Mid-April
Harp Lake	3	6.1	5.1
	3A	6.0	5.6
	5	5.9	4.8
	6	6.2	5.3
	6A	5.4	5.0
	Outflow	6.3	5.0
Dickie Lake	5	4.6	4.3
	6	4.6	4.4
	11	4.9	4.1
	Outflow	5.6	4.9
Chub Lake	1	5.8	5.1
	2	5.2	4.7
	Outflow	5.5	4.8
Red Chalk Lake	1	6.1	5.6
	2	4.5	4.3
	3	6.0	5.5
	4	6.2	5.5
	Outflow	6.1	5.9
Maple Lake	Maple Creek	6.2	5.8
Lake Simcoe	Black River (at Vankoughnet)	6.3	5.9
Lake of Bays	Oxtongue River	6.3	6.1

From: Jeffries et al., 1979

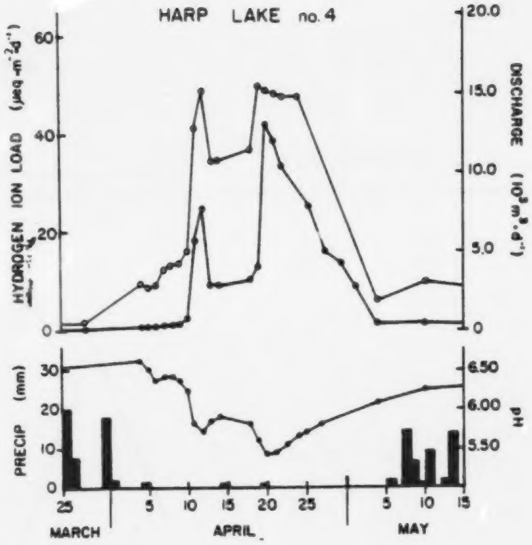

Figure 19. Discharge (○), hydrogen ion load per unit area (●), pH (lower graph), and depth of precipitation for each day that a precipitation event ocurred for Harp Lake no. 4. Daily H^+ load to the respective lakes can be calculated by multiplying by the watershed area: lake area (A_d/A_o); where A_d is the area of the subwatershed and A_o that of the lake; A_d/A_o is 1.85 for Harp Lake no. 4. From Jeffries et al. 1979.

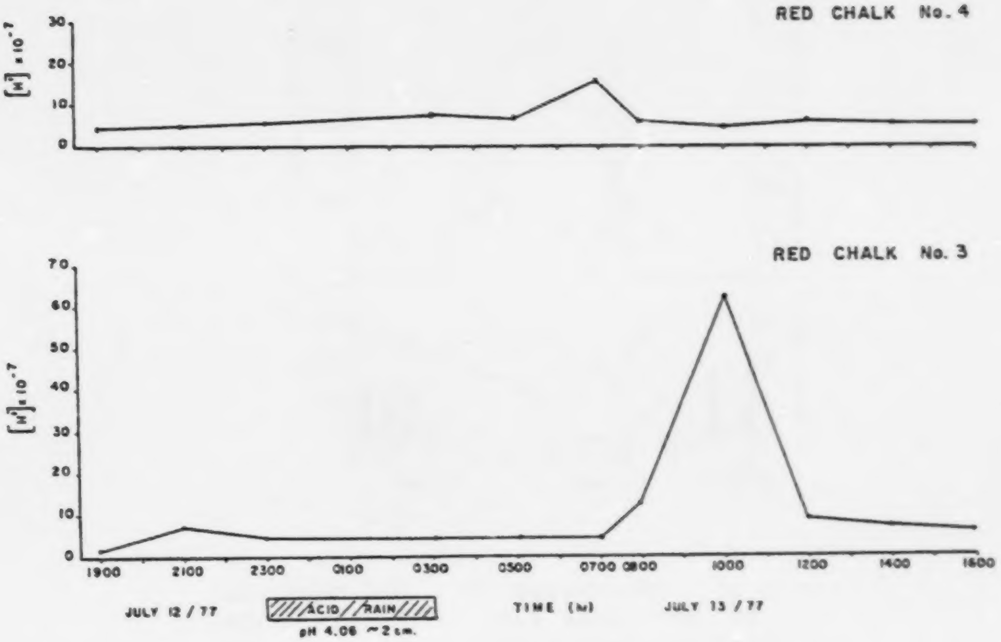

Figure 20. Hydrogen ion content of streams draining Red Chalk Lake watersheds No. 3 and No. 1 (Dorset, Ontario) showing effects of a 2 cm rainfall (pH 4.06) between 11:00 p.m. July 12, 1977 and 3:00 a.m. July 13, 1977 (Scheider et al., 1978).

Relationship of Forest Manipulation or Other Land Use Practices to Watershed Outputs

Land use practices within watersheds have been suggested as an influence on the budgets (Rosenquist, 1980; Nordquist; Henderson et al., 1980). Henderson et al., (1980) have summarized results, from watersheds at Hubbard Brook, Fernow and Coweeta, that were experimentally manipulated through a series of forest cutting practices. The work was designed to estimate changes in streamflow of cations, particularly potential effects on H^+ concentrations. At Hubbard Brook, following felling of all vegetation, and herbicide treatments for three successive years, an increase of 245.9 kg/ha of nitrogen discharges into stream flow was observed. Increased acidity from biomass decomposition amounted to 69.9×10^3 equivalents of H^+ per hectare. This additional acidity is presumed to have been a major contributor to the loss of cations from the soil, shown in Table 3-6.

Strip-cutting of one-third of the vegetation at a second Hubbard Brook watershed showed significantly less impact on soil leaching rates. Organic matter decomposition was about 5% of that of the total vegetation removal (500 kg/ha versus 10,500 kg/ha). Subsequently, H^+ production also was less, as was resultant cation leaching.

Commercial clear-cutting at the Fernow watershed generated less H^+ equivalents. This result may have been due to removal of only "economic biomass", which reduced overall decomposition rates and resultant H^+ formation. The Coweeta clear-cut and cable logging experiments resulted in even less production of H^+ ions. When the Fernow watershed was fertilized with 260 kg/ha of urea, a ten-fold stripping of calcium ions occurred, plus a 6-fold increase in magnesium, a 50% increase in potassium leaching, and a 3.6-fold increase in sodium ion denudation occurred.

Considering the oxidation of urea to be a two-step reaction yielding nitrate, and considering that four equivalents of H^+ are released per nitrate molecule, comparable leaching increase potentials were calculated for three precipitation acidity scenarios (Table 3-7). Additional H^+ inputs of 750, 3990, and 14,250 equivalents per hectare would be experienced for 150 cm of precipitation at pH 4.0, 3.5, and 3.0, respectively. At the more acidic pH values, aluminum leaching (and, therefore, buffering of effects on the other cations would be expected to increase substantially.

REGIONAL RESPONSES IN LAKE CHEMISTRY

A decade of results in Scandinavia indicate that as lakes are subjected to acidic precipitation, cations are mobilized, and that some of the bicarbonate ions are replaced by sulphate, thus, the normal relationship between the dominant cations, calcium and magnesium, and alkalinity, appears to be altered. Although these lakes are not necessarily

TABLE 3-6

SUMMARY OF TOTAL CATION RELEASE, HYDROGEN PRODUCTION AND THE CATION RELEASE RATIO FOR FIVE MANIPULATED-WATERSHED STUDIES

	H^+ produced (eq/ha)	Total cation release (eq/ha)	Cation release ratio (eq/eq/H^+)
Hubbard Brook			
Deforested	69,960	6,850	0.10
Strip-cut	8,400	390	0.05
Fernow			
Clear-cut	960	170	0.18
Fertilization	55,710	2,420	0.04
Coweeta			
Clear-cut and cable-logged	360	50	0.14

From: Henderson et al., 1980

TABLE 3-7

POTENTIAL INCREASE IN CATION LEACHING EXPECTED UNDER THREE PRECIPITATION ACIDITY REGIMES

pH	Additional H^+ (eq/ha)	Cation leaching potential (eq/ha)		
		Low	High	Median
4.0	750	30	135	75
3.5	3,990	160	720	400
3.0	14,250	570	2,565	1,425

From: Henderson et al., 1980.

acidic, the alkalinity will be less than predicted, by the sum of calcium plus magnesium.

In order to examine these relationships, a comparison of several Canadian lake studies, including the Muskoka/Haliburton area, has been summarized for many sites, inside and outside of high acid deposition areas. Those lakes from areas receiving precipitation of pH less than 4.6 fall well to the right of the equivalence line (Figure 21). These observations, in conjunction with the previous results on changes in ionic strength induced by H^+, lead to the conclusion that elevated H^+ and SO_4^{2-} additions modify the water chemistry of many aquatic ecosystems. Many of the affected lakes are not technically acidified (in the sense of depressed pH), but the long-term biological consequences of the altered water chemistry are unknown at this time. Although naturally acid lakes do occur, a significant number of seriously acidified lakes appear to be a recent response of low alkalinity systems to the continuing addition of H^+ and SO_4^{2-}.

MOBILIZATION OF METALLIC COMPONENTS OF SOIL AND SEDIMENT

One of the indirect effects of soil acidification processes is the mobilization of aluminum. The solubility of this metal is pH dependent, and increases with increasing acidity, as well as increasing alkalinity (Figure 22). Several reports have documented elevated aluminum concentrations in the surface waters of areas known to be impacted by acid inputs, (Figure 23), (Davis, 1980; Cronan and Schofield, 1979), and in effluent from lysimeters treated with acid solution (Dickson 1978; Abrahamsen et al., 1976). While aluminum ordinarily is leached from the upper soil horizon of podsol soils by carbonic acid and organic chelation, it is usually deposited in lower horizons. Under the influence of strong acids in precipitation, however, the aluminum may be mobilized in the upper (slightly acid) soil horizons and transported by saturated flow through the surface layers into lakes and streams (Hall et al., 1980; Hermann and Baron, 1980). Elevated aluminum concentrations occur during the spring melt of the snowpack, when large quantities of H^+ ions are released into the saturated surface layers (Seip et al., 1980).

The mechanism supplying Al^{3+} to soil water, and therefore to shallow inter-flow water, is the decomposition of alumino-silicates and gibbsite. Norton, (1976), and Reuss, (1976) suggest the following model:

$$Al_2Si_2O_5(OH)_4 + 6H^+ = 2Al^{3+} + 2H_4SiO_2 + H_2O$$
$$Al(OH)_3 + H^+ = Al(OH)_2^+ + H_2O$$
$$Al(OH)_2^+ + H^+ = Al(OH)^{2+} + H_2O$$
$$Al(OH)^{2+} + H^+ = Al^{3+} + H_2O$$

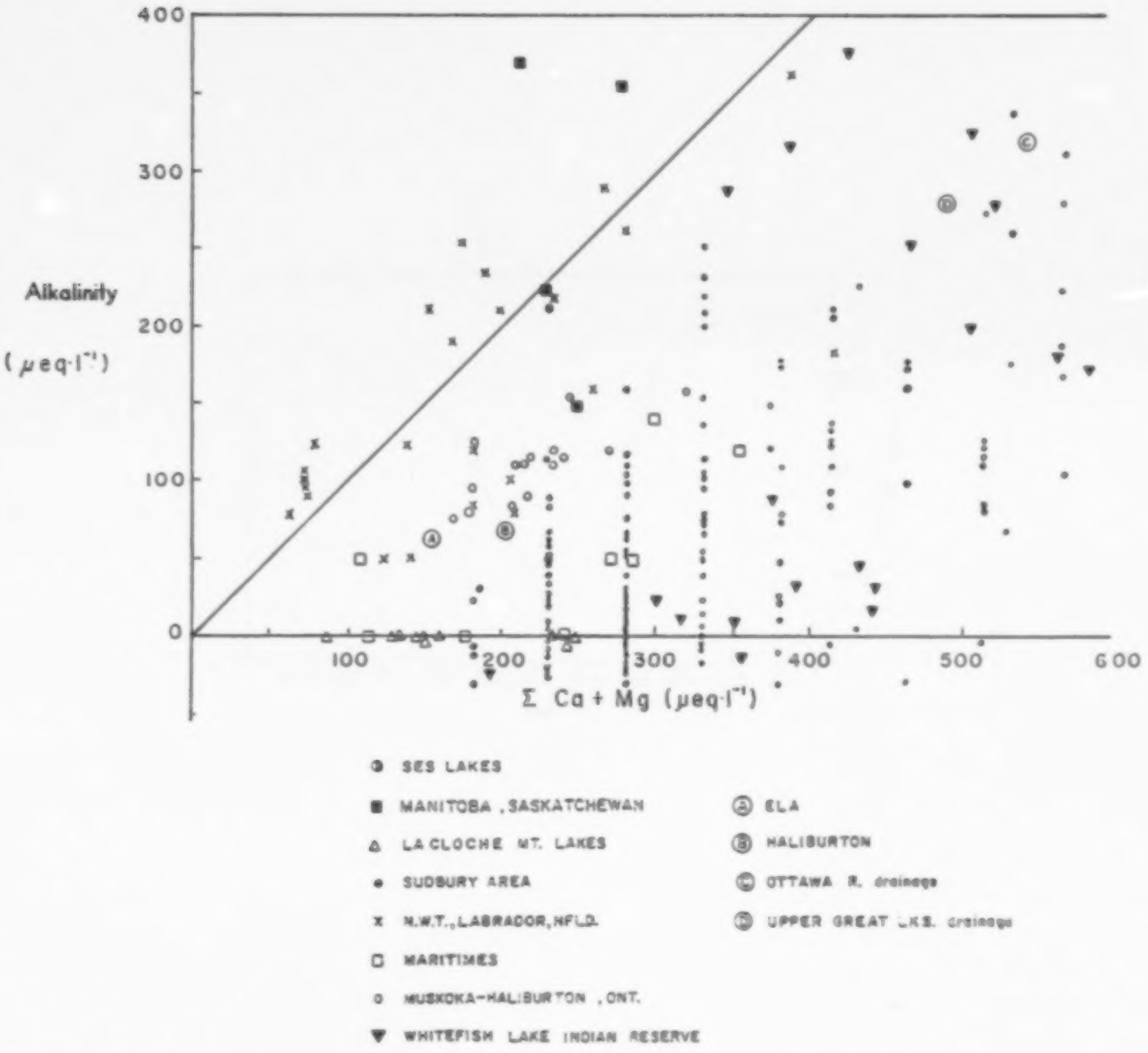

Figure 21. Summary of alkalinity data from several Canadian lake studies, including sites inside and outside of acidic deposition areas (NRC, 1980).

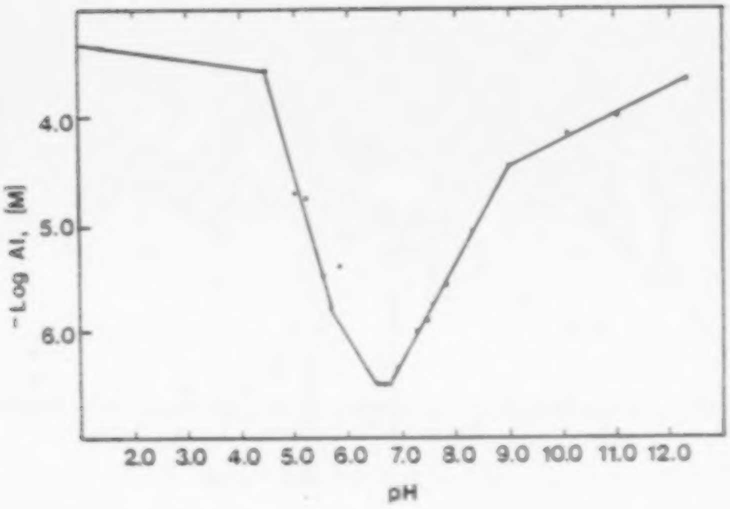

Figure 22. Relationship of aluminum concentrations to pH showing amphoteric nature of aluminum (Davis, 1980).

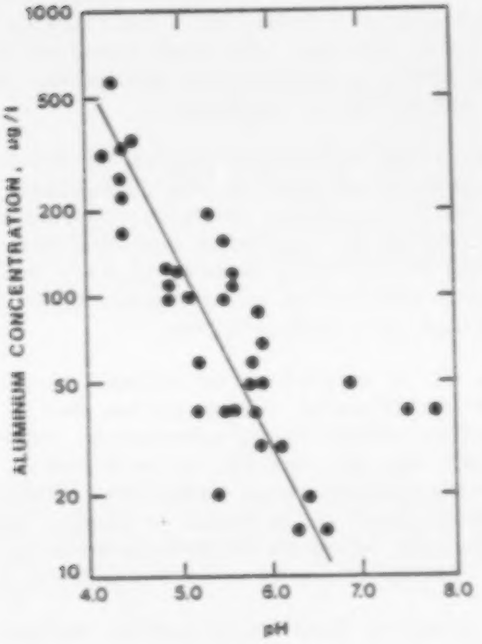

Figure 23. Relationship of observed stream concentrations of aluminum to the pH of surface water (Cronan and Schofield, 1979).

These reactions are likely to occur in watersheds where there are no carbonates to consume H^+, and the above reactions become the primary buffering mechanism (Johnson, 1979; Kramer, 1976). The pH at which this buffering occurs is around 4.5-5.0, as indicated by the Al^{3+} solubility diagram of Davis et al., 1980, which shows $Al(OH)_3$ beginning to decline rapidly at pH 5, as Al^{3+} begins to increase. The other soluble Al species, $Al(OH)_2^+$, $Al(OH)^{2+}$, and $Al_6(OH)_{15}^{3+}$, never exceed 10% of total aluminum.

In the aquatic systems, aluminum forms a variety of complexes with water and its constituents, including hydroxide, fluoride, silicate, organic matter and sulphate (Everhart and Freeman, 1973; Driscoll, 1980; Baker and Schofield, 1980). It is rarely found as the toxic free-ion. According to Johansson, (1980), these aluminum complexes act as a buffer in the pH range 4.5-5.0, but above and below these levels, buffering cannot be ascribed to aluminum complexes. Henriksen, (1980) shows that lakes with pH 4.5-4.8 are less acid than expected from a theoretical "titration" curve based on bicarbonate buffering, and that the extra buffering can be explained by aluminum.

In surface waters of the Adirondack Region of New York, Driscoll, (1980) found aluminum-organic complexes as the predominant monomeric form (average = 44%), which increased linearly with total organic carbon content. Aluminum-fluoride complexes were the most abundant inorganic form (average = 29% of the total monomeric Al), with their concentration increasing with decreasing pH, although their formation was generally limited by fluoride concentration.

A decrease in the pH of natural water columns has been shown to cause substantial increases in metal concentration due to their release from sediments. Schindler (1980) found substantial increases in lake water concentration of Al, Mn, Zn, and Fe, at pH 6 and 5, in an experimentally acidified lake in the Experimental Lake Area. Zinc concentrations at pH 5 exceeded levels found to be toxic to fish. Also, radionuclides of Fe, Co, Mn, and Zn were found to be more soluble in acidified systems, whereas Hg and V radionuclides were less soluble.

ACID-INDUCED MOBILIZATION FROM SOLID WASTES, METALS AND MINE TAILINGS

Acid deposition is known to affect steel, copper, galvanized sheet and other metals, stone, paints, and plastics, both through dry and wet deposition. Exposure to atmospheric sulphur compounds can cause scaling and loss of surface cohesion in limestone and sandstone.

Thus, the effects, for aquatic resources, of acidic rainfall on construction materials, such as roofing, can be of importance to water quality. Similarly, materials in solid waste disposal sites, mine tailing disposal sites, and other materials, may be influenced more by acidic rainfall and runoff than by relatively neutral rain. The magnitude of these effects is not known at this time.

ALTERATION OF IMPACTED BIOTIC COMPONENTS

Acidification of lakes and rivers has the potential to reduce the number of species, and, in some cases, the total number of aquatic organisms. The remaining species may not be suitable as food for the normal predators, so the food chain is disrupted, resulting in further alterations of species composition of the aquatic ecosystem.

Phytoplankton

Acidification of freshwater alters the metabolism of both attached and free-floating algae, resulting in diminished populations of some species and increased populations of others. Generally one or two highly dominant (acidophilic) species emerge, thus changing species diversity. Changing species composition, as acidity increases (from chrysophytes and diatoms to dinoflagellates, and from larger to smaller sizes), leads to selective changes in zooplankton diversity, due to changes in edible food (see zooplankton section). The final effect of this food chain modification can be expected in the altering of normal fish diversity and abundance.

Evidence from Scandinavia, Canada and the United States has documented decreasing species diversity of attached and free- floating algae, with increasing acidity, although Crisman et al., (1980) found no relationship between lake pH and numbers of phytoplankton species in 20 Florida Lakes over a pH range of 4.5-7.0. Although species diversity generally decreases with acidity, overall biomass often remains unchanged, or even increases, because of less competition for available nutrients. Phosphorus is a nutrient that can determine phytoplankton productivity, and, due to immobilization reactions this nutrient can become less available as pH drops below 6.0.

In Sweden (Grahn et al.,1974), and in Ontario (Ontario Ministry of the Environment, unpublished), acidified lakes containing unusually dense and extensive beds of periphyton (*Mougeotia* and *Zygogonium* sp.) in littoral zones have been found. Yan and Stokes, (1976) observed only nine species of phytoplankton in a single sample from Lumsden Lake (pH 3.8), in the LaCloche Mountains in Ontario, but over 50 species in each of two nearby non-acidic lakes. Diversity indices for the LaCloche Mountain lakes decrease sharply as pH falls below 5.6 (Kwiatkowski and Roff, 1976), while species numbers decrease most rapidly at a pH level of about 5.5 in Scandinavian lakes (Almer et al., 1978; Leivestad et al., 1976).

Phytoplankton communities of non-acidic oligotrophic lakes in eastern Canada are typically dominated by chrysophytes (Schindler and Holmgren, 1971), or by diatoms (Duthie and Ostrofsky, 1974).

In contrast, strongly acidic lakes are generally dominated by dinoflagellates. In Sweden, the Pyrrhophyta, especially the dinoflagellates, formed 85% of the biomass in lakes of pH 4.6-5.5 (Dickson et al., 1975). Of 14 lakes in central Ontario, dinoflagellates formed between 30 and 70% of the phytoplankton biomass in four acidic lakes (pH 4.2-4.8), but only 2-30% of the biomass in ten lakes with pH levels of 5.8-6.8 (Yan, 1979). As a group, dinoflagellates cannot readily be ingested by zooplankton; thus changes in phytoplankton species diversity can affect the zooplankton food base.

At earlier stages of the acidification process, many taxa other than dinoflagellates, may become dominant for periods of time. Some of the species may interfere with recreational use of the lakes. In five lakes in Ontario and New Hampshire in the range of pH 5.5 to 6.2, for example, obnoxious odours developed during the summers of 1978, 1979, and 1980. The odours have been shown to be caused by the growth of the planktonic prymnesiophyte Chrysochromulina breviturrita. This species was first discovered in 1976, but it is now known to inhabit more than 40 lakes in Ontario, most of which are acidic (Nicholls et al., 1980). The "invasion", and associated odour production, by this organism is apparently a recent phenomenon. Although the relationship between lake acidification and the proliferation of this species has not been proven, data collected thus far show that the growth of this species, and the serious odour production, is restricted to acidic lakes.

Some long-term functional adaptation by algae to acidic environments has been suggested by Raddum et al., (1980). Their results showed that a group of relatively recently acidified clearwater lakes had lower numbers of species than acidic humic lakes, which had been acidic for much longer periods of time.

Data on phytoplankton populations since the late 19th century, based on paleo- ecological studies of diatom casings in the upper sediment layers of acid lakes in New York and Maine, indicate changes in phytoplankton species composition similar to those associated with recent changes in lake pH's. These data suggest that the earliest expression of the acidification process in the most sensitive lakes began late in the 19th century. These results are consistent with the eariest observations of fish-kills in Norway (1914-1922), now believed to be attributable to flushing of acid accumulated in snow.

Aquatic Macrophytes

With the exception of some documented studies of Swedish Lakes (Grahn et al., 1974; Hultberg and Grahn, 1976; Grahn, 1976; Hendrey et al., 1976), there is little information on the effects of increasing acidification on the macrophyte communities of soft water lakes. Evidence available from Scandinavia suggests that increasing acidity leads to a plant succession which tends to reduce aquatic macrophytes and replace them with dense growths of Sphagnum mosses. The decline in macrophyte species, and correlative increase in Sphagnum sp., appear to be dependent on factors which are directly or indirectly associated with pH changes of the water: i.e. the state of the hydrogen carbonate buffer system (Steeman-Nielson, 1944, 1946; Ruttner, 1948).

The decline of macrophyte species and resulting invasion of Sphagnum mosses begins around pH 6.0, but increases markedly below pH 5.0. Such growth has been observed in Lake Cullen (pH 4.9), New York (Hendrey and Vertucci, 1980), while recent surveys of Ontario Precambrian Shield lakes identified some Sphagnum mosses (Wile, unpub. data). However, no growth of the magnitude reported in Scandinavia has been observed to date.

While little concrete evidence exists, one can hypothesize as to the possible consequences of macrophyte succession and Sphagnum invasion in acidic lakes. Sphagnum moss is known for its ion exchange capacity and its ability to remove cations such as Ca^{2+}, Mg^{2+}, Fe^{2+}, Na^{+}, and K^{+} from the aquatic media in exchange for H^{+} (Hultberg and Grahn, 1976; Crum, 1976; Clymo, 1963). In addition to reducing the availability of cations essential for biological production, this ion exchange process may further increase acidity in the microenvironment surrounding Sphagnum beds.

Wium-Anderson and Anderson, (1972) have demonstrated that some soft-water macrophyte species, absorb free carbon dioxide from the sediment and release O_2 through their roots (as their stomata are missing), thus assisting in oxygenation of the sediments. Inhibition of these macrophytes, by the direct or indirect effects of acidification could potentially affect decomposer organisms by limiting the availability of oxygen (Laake, 1976; Leivestad et al., 1976).

In many Scandinavian macrophyte studies (Grahn et al., 1974; Hultberg and Grahn, 1976; Hendrey et al., 1976; Almer et al., 1974), a marked increase in the growth of periphytic algae has occurred. Similarly, in New York State (Hendrey and Vertucci, 1980), unusual accumulations of both epiphytic and epilithic algae under acid conditions have been reported. Growth of acid tolerant species has been observed to cover macrophytes completely in some areas of the lake, thus preventing the capture of sunlight by the macrophytes. The macrophytes are unable to grow without sunlight.

In many Scandinavian lakes studied to date, an increase in bottom accumulation of organic material has been observed. This has been attributed to a shift in dominance from bacteria to fungi, thus retarding the rate of decomposition and delaying the recycling of nutrients. This further accelerates the acidification process (Grahn et al., 1974; Hultberg and Grahn, 1976).

Finally, Sphagnum moss coverage of littoral zones creates a unique habitat which is considered unsuitable for some species of benthic invertebrates, or for use as fish spawning and nursery ground (Hultberg and Grahn, 1976). Additionally, dense beds of Sphagnum and filamentous algae may reduce the appeal of freshwater systems for certain recreational activities.

Effects on Zooplankton

Zooplankton are the smallest metazoans (multi-cellular animals) in lakes, ranging in size from about 0.05 to 10 mm. Four major groups of animals contribute to zooplankton communities: protozoans, rotifers, crustaceans and insects. They provide food for many species of fish, particularly for younger individuals, and thus are an essential component of the aquatic food chain, transferring energy and materials from the primary producers (algae) to consumers, including fish and man.

The most important components of zooplankton communities are usually the rotifers and crustaceans. Of these, the crustaceans usually form >90% of the biomass (Pederson et al., 1976), while rotifers, because they have shorter generation times, may be responsible for <50% of the zooplankton productivity (Makarawicz and Likens, 1979). Studies from acid-mine drainage lakes indicate that some species of rotifers can survive when all crustacean zooplankton have been eliminated by acidification (Smith and Frey, 1971). Thus, rotifers may become more important contributors to the zooplankton community, as lakes acidify. Available studies on the effects of acidification on rotifer populations are contradictory: both decreases (Roff and Kwiatkowski, 1977) and increases (Yan, in press) in standing stocks have been observed in acidic lakes.

Acidification of lakes is accompanied by changes in the occurrence, abundance and seasonal succession of species, and in the diversity of crustacean (and other) zooplankton components. It is often assumed that the direct cause of these changes is differences in tolerance, among zooplankton species, to increased H^+ concentration. However, acidification also increases the transparency, thus affecting the light regime, of lakes (through effects on algae), increases the concentration of chemical substances, including potential toxicants, and produces quantitative and qualitative changes in zooplankton predator and prey species (Sprules, 1976). Hence, the immediate causes for the changes in zooplankton communities that do occur, while linked to acidification, may be quite complex.

Changes in phytoplankton community structure induced by acidification, may also significantly alter zooplankton community structure. In acidic lakes, dinoflagellates, a group generally not ingestible by zooplankton, contribute much more to total biomass than in non-acidic lakes.

Future studies should be conducted to confirm that acidification interrupts food chain processes.

Effects on Aquatic Macroinvertebrates

Numerous aquatic macroinvertebrates are known to be affected by the acidification of water. While in some cases an entire phylum appears to be affected, in other situations susceptibility is species specific. Evidence indicates that molluscs, in general, are highly susceptible to pH change (Raddum, 1980; Okland, 1980; Wiederholm and Eriksson, 1977), often being restricted to habitats with pH greater than 5.8 to 6.0. Similarly, oligochaetes have been found at lower densities in acid waters (Wiederholm and Eriksson, 1977).

The classes of arthropods which have been studied for the effects of acid precipitation include Arachnida, Crustacea and Insecta. Arachnids were only briefly mentioned by Grahn and his co-workers (1974): acarina were absent in waters with pH values below 4.6. No members of the crustacean class were found below pH 4.6 (Grahn et al., 1974). In this group, organisms affected by acid precipitation range from amphipods to crayfish. Gammarus lacustris was absent from waters with pH below 6.0 (Okland, 1969), while the crayfish, Astacus astacus was rare in lakes where the summer pH value was less than 6.0 (Svardson, 1974).

Orders of Insecta exhibit a wide range of sensitivities to pH. While the number of species of Ephemeroptera and Plecoptera appear to be positively correlated with pH, larvae of Chironimida, Hemiptera and Megaloptera are often abundant in acid lakes (Almer et al., 1978).

Although the field studies mentioned above provide evidence of the effects of acidification on certain species, in only three studies has the pH of a natural system been altered, and the impacts on invertebrates noted. The documented effects of decreased pH include the disappearance of Mysis relicta in an acid treated lake in the Experimental Lakes Area (W. Nero, personal communication), elimination or reduction of Ephemeroptera populations in the Hubbard Brook Experimental Forest in New Hampshire (Fiance, 1978; Hall et al., 1980), and decreased emergence of some species of Plecoptera, Trichoptera and Diptera, also at Hubbard Brook (Hall et al., 1980).

Those species with acid-sensitive life stages (such as emergence in insects) that can coincide with snowmelt or other events, such as flushing, may be especially sensitive to acid precipitation.

It is important to note, in considering the distribution of the above species in relation to waters of varying pH, that no causative relationship between hydrogen ion concentration and the observed changes has been determined as yet. Other factors vary with pH, including concentrations and availability of nutrients, bicarbonate and sulphate ion, and various metals, as well as organic contaminants. From the results available, however, it appears that shell-bearing organisms (perhaps because of their requirement for calcium), and moulting crustaceans (perhaps because of the calcium dependence of the moult), are the most sensitive macroinvertebrates to low pH levels. It is still unclear why certain groups of aquatic insects are more sensitive than others.

Effects on Microorganisms

The decomposition of fixed carbon, both allochthonous and autochthonous organic matter, is in large part determined by microbial processes in the water column and in the surface layers of sediment. Several studies have demonstrated that rates of decomposition of organic matter are decreased in acidified waters. In a laboratory study, for example, Bick and Drews (1973) demonstrated that as pH was lowered, the number of bacteria and protozoans decreased, populations of fungi increased, and the rates of decomposition and nitrification were reduced. Traaen, (1980) measured decomposition rates of homogenized birch litter and glucose/glutamate mixtures. When the pH was decreased from 7.0 to 3.5, litter decompostion dropped to 30% of control levels, and a shift from bacterial to fungal dominance was observed. In contrast, long-term experiments by Traaen found significantly higher losses of weight in substrates placed in acidified (pH 4-5), compared with non-acidified, lakes or streams.

As rates of decomposition are reduced, organic debris accumulates and nutrient cycling may be inhibited. This may interfere with nutrient supplies for plants. Reduction in bacterial numbers and biomass may also affect invertebrates, which prefer conditioned (colonized by bacteria) detritus.

Reductions in numbers of heterotrophic bacteria have been observed previously in aquatic habitats acidified by acid mine drainage (Tuttle et al., 1968, 1969; Thompson and Wilson, 1975; Guthrie et al., 1978). Caution must be exercised in extrapolating results from acid mine drainage studies to situations where the source of protons is the atmosphere, however, although bacterial numbers are reduced in both situations. Field experiments in Norway (Traaen and Laake, 1980) demonstrated that, as pH decreased from 6.1 to 4.0, bacterial diversity was reduced, community respiration decreased, and a possible inhibition of nitrification occurred.

Microbial transformations of sulphur and nitrogen species may also influence lake alkalinity (Brewer and Goldman, 1976). Schindler (1980) recently suggested that increases in SO_4^{2-} concentrations will stimulate sulphate-reducing bacteria in lakes that develop anoxic hypolimnia. He further speculated that methanogenic bacteria would be replaced by sulphate-reducing bacteria under these conditions. The reduction of SO_4^{2-} generates bases, i.e. it increases alkalinity. Stimulation of SO_4^{2-} reduction has been used with success to renovate acid mine drainage waters. However, sulphate-reducing bacteria require anoxic conditions, and are stimulated by large quantities of organic matter, i.e., they require conditions typical of eutrophic lakes. Stimulation of SO_4^{2-} reduction is, therefore, unsuitable as a renovative tool for acidic lakes. Eutrophication seems not to be a satisfactory trade-off for reducing acidity.

Studies of pH effects on ammonifiers, denitrifiers, fungi and heterotrophs, in Sudbury area lakes acidified to pH 4.1, have been measured. A decrease in nitrogen cycle bacteria is being observed in the lake under investigation, with no finding of sulphur cycle bacteria. Laboratory studies indicate no change in heterotroph levels, a doubling in numbers of fungi, a decrease in nitrogen cycle bacteria up to twofold, and a significant decrease in respiraton rate (R.H. Rao, personal communication).

Effects on Amphibians

Many species of frogs, toads and salamanders breed in temporary pools. The pH of these pools may be very low during the spring, as they are formed primarily by meltwater. Pough and Wilson, (1977), for example, found mean pH values of 4.5 in the temporary pools used by Jefferson and spotted salamanders as breeding sites. Nearby, permanent pools had much higher mean pH values of 6.1. Like fish, amphibians are particularly sensitive during early embryonic stages. It has been shown that embryonic development is greatly retarded in certain species of amphibians when pH falls below 6.0 (Pough and Wilson, 1977). Because of the vulnerability of their habitat to pH depressions, damage to amphibian populations may be one of the earliest consequences of acidification of fresh waters. Reductions in the biomass of amphibians could have far-reaching effects in both aquatic and terrestrial ecosystems. Because salamanders and frogs are important components of the food web, higher orders of wildlife, such as birds and mammals, depend heavily on these species for food.

Amphibians are also important predators of aquatic insects and are among the top carnivores in pond and stream ecosystems (Orsen and Shure, 1972). These species, in turn, serve as a high protein food source for other wildlife. Species in eastern North America that are most susceptible, because of their breeding habitat, are listed in Table 3-8. Sensitivity is inferred from field investigations, and has been demonstrated in laboratory studies. No field studies have been conducted, in which stream or lake pH was artificially acidified, to determine effects on amphibians.

In field surveys in central Ontario, Clark and Fischer (in preparation) found that male calling densities (an estimate of population size) of spring peepers and numbers of egg masses of Yellow-spotted salamanders (Ambystoma maculatum), were positively correlated with pH. Pough, (1976) noted heavy embryonic mortalities and deformities in Yellow-spotted salamanders at pH values less than 6.0. Similarly,

TABLE 3-8

SUSCEPTIBILITY OF BREEDING HABITAT TO pH DEPRESSION DUE TO ACID PRECIPITATION, FOR THOSE AMPHIBIANS IN CANADA WHOSE RANGE OVERLAPS THE IMPACTED AREA

Potential for acidification of egg-laying habitat	Habitat	Species
high	meltwater pools	Ambystoma maculatum - Yellow-spotted salamander
		Ambystoma laterale - Blue-spotted salamander
		Ambystoma tremblayi - Tremblays salamander
		Bufo americanus - American toad
		Pseudacris triseriata - Chorus frog
		Rana sylvatica - Wood frog
		Hyla crucifer - Northern spring peeper
moderate	permanent ponds	Necturus maculosus - mudpuppy
		Notophthalmus viridescens - Red-spotted newt
		Hyla versicolor - Gray tree frog
		Pseudacris triseriata - Chorus frog
		Rana clamitans - Green frog
		Rana pipiens - Northern leopard frog
		Rana septentrionalis - Mink frog
	streams	Eurycea bislineata - N. two-lined salamander
	lakes	Rana catesbiana - Bullfrog
low	bogs	Hemidactylium scutatum - Four-toed salamander
	logs and stumps	Plethedon cinerus - Red-backed salamander

From: Clark and Fischer (in preparation)

Strijbosch, (1979) reported a negative correlation between pH and percentages of dead and moulded egg masses of frogs and toads in the Netherlands. From studies in ponds in England, Cooke and Frazer (1976) reported that no adult newts were caught from ponds of pH <3.8. The common toad did not occur where pH values were <4.2, and the smooth newt rarely occurred at pH values <6.0. Hagstrom, (1977) observed that the common toad and common frog disappeared when pH levels reached 4.0-4.5.

Laboratory investigations have demonstrated that reductions in pH are, directly or indirectly, responsible for the losses of these populations. Gosner and Black, (1957) studied the sensitivity of 11 species of frogs and toads to conditions of depressed pH. They found that the embryos were more sensitive than larvae or adults. In the cricket frog and northern spring peeper, an exposure of embryos to water of pH =4.0, for a few hours, resulted in greater than 85% mortality. In salamanders, the highest mortality of developing embryos occurs during neurulation, the late stages of gill development, and during hatching (Pough, 1976; Pough and Wilson 1977).

Given this sensitivity of amphibians to depressed pH, it is inevitable that those species inhabiting temporary pools will suffer severe decreases in density, and may become locally extinct in many regions of the Canadian Shield. The ranges of some species of amphibians in eastern North America are restricted almost entirely to areas presently impinged by high levels of acid precipitation.

Impacts on Fish

The purpose of this section is to briefly review how fish respond to increasingly acidic environments. For more comprehensive treatments of this subject the reader is referred to reviews by Fromm, (1980) and, especially, Spry and Wood, (1980).

There is extensive literature available on laboratory studies (see Doudoroff and Katz, 1950, and EIFAC, 1969) designed to elucidate mechanisms of pH toxicity. These laboratory results are reviewed, as they can be useful in explaining field observations, as well as suggesting new field studies.

Much of the early laboratory work (and many of the recent efforts), describing the effects of low pH on fish, has been misleading, as the pH levels studied were generally acutely lethal, measured with variable accuracy, or did not account for such important variables as dissolved CO_2, temperature and water quality in general.

However, laboratory studies are useful in showing how overall water quality (hardness and ionic strength) can affect pH toxicity. Increasing hardness and ionic strength appears to decrease partially the sensitivity of adult fish to very acid waters (i.e. at pH 4). This ameliorative effect is most evident in the early larval stages at intermediate pH (5.0) (Spry and Wood, 1980). This is consistent with field observations that fish disappear at higher pH levels, in the more dilute waters (Leivestad and Muniz, 1976), due to recruitment failure (Harvey, 1979). Other water quality considerations which can affect survival, as related to pH, are the level of dissolved CO_2 in the water (Neville, 1979), temperature (Kwain, 1975; Robinson et al., 1976), and the type of acid (Packer and Dunson, 1972; Swartz et al., 1978). Some authors have reported that certain species are more susceptible to pH depression at different times of the year (Lloyd and Jordan, 1964; Falk and Dunson, 1977). In addition to interspecific differences in sensitivity, variability between strains of the same species has been documented (Robinson et al., 1976; Swartz et al., 1978). However, it is probable that the acidification of lakes and rivers in North America is proceeding too rapidly to allow genetic selection for acid tolerant strains to occur naturally, on a wide scale (Schofield, 1976).

Laboratory studies have indicated that fish are particularly sensitive to low enviromental pH in their reproductive phases. Low pH can inhibit gonadal development, and also reduce egg production and egg and sperm viability, resulting in reduced spawning success. The fry are often more sensitive to acid stress than are eggs, particularly at pH's near 4.0 (reviewed in Fromm, 1980, and Spry and Wood, 1980). Consequently, fry are particularly vulnerable to the low pH episodes associated with spring meltwater or storm events.

In the field, there have been several reports of fish kills apparently caused by acidification of rivers and lakes. For example, Jensen and Snekvik, (1972) report mass mortality of Atlantic salmon, and Leivestad and Muniz, (1976) report a brown trout kill. Both fish kills have been attributed to low pH. In North America, Harvey (1979) has reported a kill of several species, primarily pumpkinseeds, from Plastic Lake in Ontario, during the spring snow melt.

Results from field studies also suggest that the effects of chronic pH toxicity follow a predictable sequence of events. Decreased pH is often more destructive to younger life stages, and may cause reproductive failure (Beamish and Harvey, 1972), so that a population will first suffer from low pH by having reduced recruitment. As the pH decline continues, a total failure of one or more year classes may occur as illustrated by Ryan and Harvey's study of yellow perch in Patten Lake, in the LaCloche Mountains (Figure 24) (Harvey, 1979). Superficial examinations of these populations may be very misleading as the average size of the surviving population may actually be increasing, possibly due to reduced competition for food (Ryan and Harvey, 1980).

The susceptibility to low pH appears to be species specific. From his studies in the LaCloche Mountain lakes, Beamish estimated the pH at which reproduction ceased in 11 species, (Table 3-9), (Beamish, 1976).

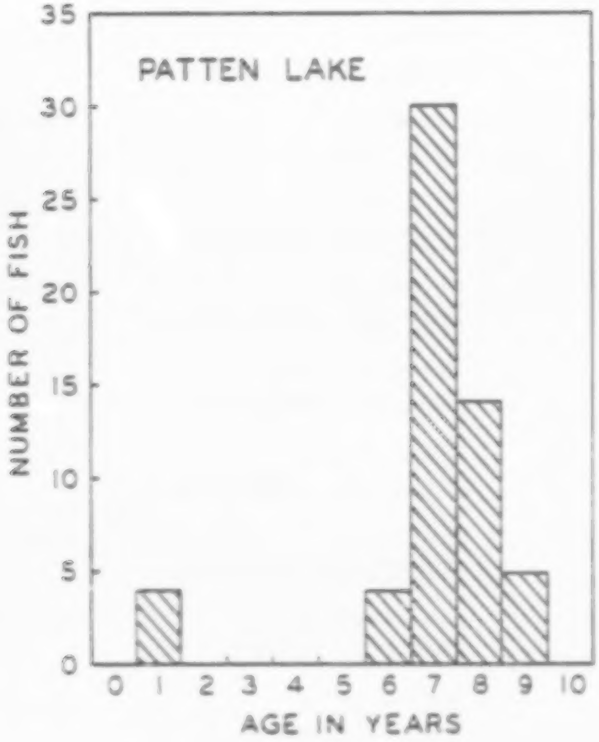

Figure 24. Age composition of yellow perch captured in Patten Lake, Ontario (Ryan and Harvey, 1980).

TABLE 3-9

APPROXIMATE pH AT WHICH FISH IN THE LACLOCHE MOUNTAIN LAKES STOPPED REPRODUCTION

pH	Species	Family
6.0 to 5.5	Smallmouth bass *Micropterus dolomieui*	Centrarchidae
	Walleye *Stizostedion vitreum*	Percidae
	Burbot *Lota lota*	Gadidae
5.5 to 5.2	Lake Trout *Salvelinus namaycush*	Salmonidae
	Troutperch *Percopsis omiscomaycus*	Percopsidae
5.2 to 4.7	Brown bullhead *Ictalurus nebulosus*	Ictaluridae
	White sucker *Catostomus commersoni*	Catostomidae
	Rock bass *Ambloplites rupestris*	Centrarchidae
4.7 to 4.5	Lake herring *Coregonus artedii*	Salmonidae
	Yellow perch *Perca flavescens*	Percidae
	Lake chub *Couesius plumbeus*	Cyprinidae

From: Beamish, 1976.

Results from Studies of Al^{3+}

Another potential adverse physiological stress associated with low pH, is heavy metal and aluminum toxicity. Levels of heavy metals are frequently elevated in acidic lakes (Schindler et al., 1979). The source of the metals may be atmospheric deposition, but, more commonly, the increases in concentration are attributable to increased mobilization of metals from lake sediments or watershed minerals. Certain metals are more toxic to fish than others, and the toxicity of a specific metal is dependent upon its speciation. The ionic fractions are generally most toxic. Metals can affect osmo- and ionoregulation, calcium metabolism, oxygen transport, and, possibly, the susceptibility of fish to disease (Spry and Wood, 1980).

Cronan and Schofield, (1979) noted that pH levels, which are otherwise not directly harmful to fish, are toxic if levels of aluminum are elevated. Aluminum toxicity to fish is exerted at the level of the gill, and may involve damage to respiratory epithelium, in addition to osmoregulatory disturbances (Muniz and Leivestad, 1980; Schofield and Trojnar, 1979). The speciation, and hence the toxicity of aqueous aluminum, is controlled primarly by pH and the concentrations of potential ligands (fluoride and organic complexes). Aluminum is most toxic in the hydroxyl forms at around pH 5. Aluminum complexed by organic matter is not toxic to fish (Driscoll, et al., 1980).

Schofield and Trojnar, (1979) indicated that levels of aluminum, rather than pH alone, may be the primary factor limiting survival of brook trout stocked in acidified Adirondack lakes. Muniz and Leivestad, (1980), and Schofield and Trojnar, (1979) suggest that mass mortalities of fish, observed during transient episodes of acidification in the spring, are most likely a result of elevated concentrations of inorganic aluminum, mobilized from the soils by strong acids present in snowmelt water. The former study clearly demonstrated that pH depression alone (to levels of pH 4.7-5.0) did not induce physiological stress to fish, as determined from changes in plasma chloride levels. However, associated increases in aluminum to 0.2 mg/l or more were found to be sufficient to induce severe stress and eventual mortality.

Mercury in Fish

Several investigations have demonstrated that concentrations of mercury in fish are higher in acidic than in non-acidic lakes (Fagerstrom and Jernelov, 1972; Brouzes et al., 1977; Hikanson, 1980). The reasons for this are not completely understood. Factors that might influence this observed phenomenon in acid sensitive lakes include: (a) the possibility that each lake has a different methylating pathway; (b) different chemical and physical partitioning of the mercury species; (c) different food chain dependents; and (d) different atmospheric deposition regimes.

Few trends in time data exist. However, an increase in concentrations of mercury in fish from 1970 to 1978 is evident in some lakes in the Adirondack Mountains (C.L. Schofield, personal communication).

In Ontario, Suns et al., (1980) have been sampling young-of-the-year and yearling fish for contaminant studies. Their data (Figure 25), demonstrated increased mercury concentrations with decreasing pH in lakes in the Haliburton area. For lakes with similar pH, the mercury was higher in fish from lakes with a higher ratio of drainage area/lake volume. This result implies that the quantity of mercury from either direct atmospheric deposition, or from watershed leaching, is influencing the fish concentrations. In 1980, the survey was extended to include adult bass, which are important to the sport fishery. Bass, from six of the nine lakes studied, had average mercury concentrations above the Canadian guideline for unlimited human consumption of 500 ng/g, and, in one lake, exceeded the U.S. guideline of 1000 ng/g (K. Suns, personal communication).

Prior to their extinction, attributable directly or indirectly to depressed pH, fish may concentrate mercury in their flesh to levels greater than under non-acid stressed conditions. Fish-eating birds and mammals may, therefore, ingest quantities of mercury which will accumulate in their tissues and exceed safe levels for human consumption. Wildlife themselves, may suffer reproductive losses from elevated levels of mercury.

Fisheries Impacts in Canada and the United States

Fisheries impacts in the Adirondacks: The Adirondack region represents one of the largest sensitive lake districts in the eastern United States, and it is also the most heavily impacted by acid precipitation. A recent inventory of Adirondack waters, classified by type of fishery supported, indicates that the brook trout fishery has been most severly affected by acidification (Pfeiffer and Festa, 1980). These authors have shown that at least 180 former Adirondack brook trout ponds will no longer support populations, because of acidification. Currently, 212 Adirondack lakes have a pH <5.0, and an additional 256 lakes have a pH between 5.0 and 6.0. A survey of 214 lakes in 1975 by Schofield, (1976), revealed that 52 per cent had surface pH levels below 5.0, and 90 per cent of these acidified lakes were devoid of fish life (Table 3-10). Comparable data collected for 40 of these lakes, from the period 1929 to 1937, indicated that only four per cent were below 5.0 and devoid of fish (Figure 26). Entire fish communities, consisting of brook trout, lake trout, white sucker, brown bullhead and several cyprinid species, were eliminated over the forty year period, in association with decreased pH. The number of fish species represented in these high elevation lakes was also observed to decline markedly below pH 5.5.

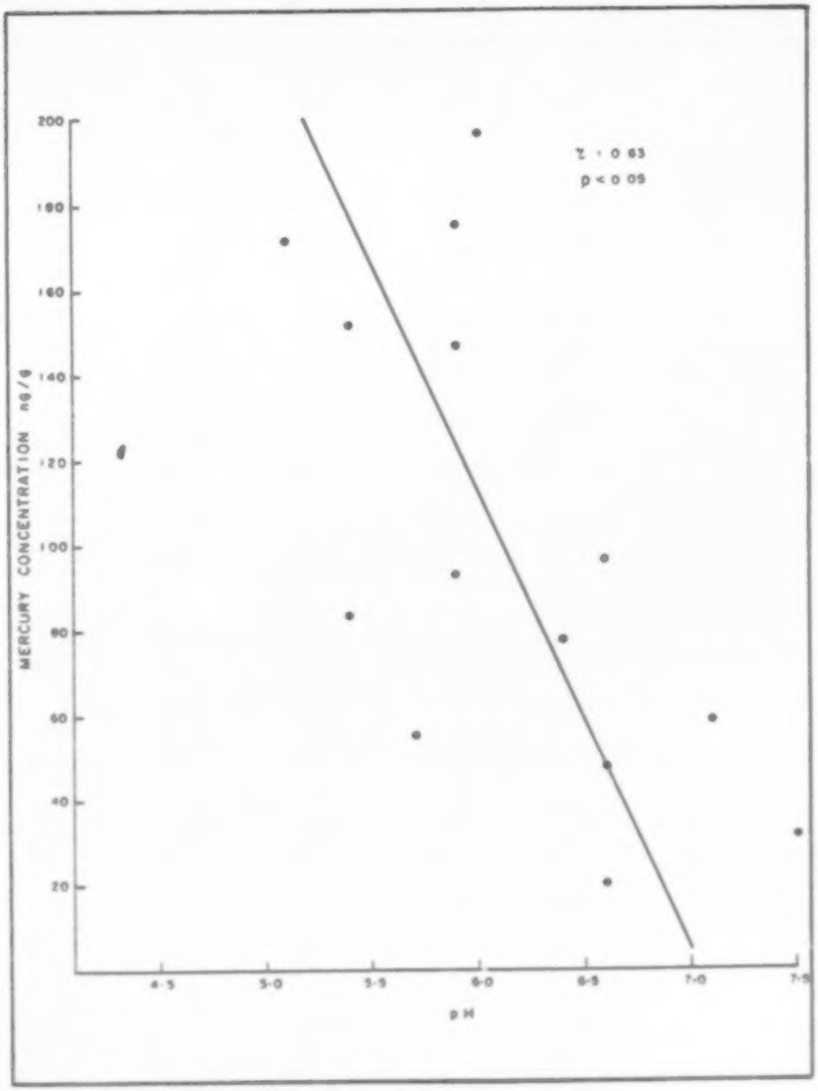

Figure 25. Mercury concentrations in yearling yellow perch and epilimnetic pH relationships (Suns et al., 1980).

TABLE 3-10

DISTRIBUTION AND FREQUENCY OF OCCURRENCE OF FISH SPECIES COLLECTED DURING SURVEYS OF ADIRONDACKS LAKES >610 METERS ELEVATION

NUMBERS IN ( ) REFER TO EXTINCT POPULATIONS

pH	<4.5	4.5-4.99	5.0-5.49	5.5-5.99	6.0-6.49	6.5-6.99	>7.0	TOTAL
Total lakes	16	95	36	15	28	22	3	215
Percent of total	7.1	44.2	16.7	7.0	13.0	10.2	1.4	
No fish	16	74	2	1	0	0	0	93
Percent	17.2	79.6	2.1	1.1				
Fish	0	20	25	11	22	19	3	100
Percent		20.0	25.0	11.0	22.0	19.0	3.0	
Brook trout	0	16(26)	18(1)	11	17	17	3	82
Percent		19.5	21.9	13.4	20.7	20.7	3.7	
f	.80	.72	1.00	.77	.89	1.00		
Lake trout	0	0(5)	1(2)	4	2	4	2	13
Percent			7.7	30.8	15.4	30.8	15.4	
f			0.4	.36	.09	.21	.67	
Bullhead	0	8(8)	11(1)	5	14	9	3	50
Percent		16.0	22.0	10.0	28.0	18.0	6.0	
f		.40	.44	.45	.64	.47	1.00	
White sucker	0	3(1)	7(1)	8	7	8	3	36
Percent		8.3	19.4	22.2	19.4	22.2	8.3	
f	.15	.28	.73	.32	.42	1.00		
Creek chub	0	0(7)	5	7	5(1)	8	2	27
Percent			18.5	25.9	18.5	29.6	7.4	
f			.20	.64	.23	.42	.67	
Golden shiner	0	3(4)	3	1	8	3	2	20
Percent	15.0	15.0	5.0	40.0	15.0	10.0		
f	.15	.12	.09	.36	.16	.67		
Common shiner	0	9(2)	0(1)	3(1)	1	3	3	11
Percent		9.1	0	27.3	9.1	27.3	27.3	
f		.05		.27	.05	.16	1.00	
Lake chub	0	1(1)	0	2	0	1	3	7
Percent		14.3		28.6		14.3	42.9	
f		.05		.18		.05	1.00	
Redbreast sunfish	0	0	0	0	0	3	0	3
Percent						100.0		
f						.16		
Common sunfish	0	0(1)	0	1	1	2	2	6
Percent				16.7	16.7	66.7	66.7	
f				.09	.05	.11	.67	

From Schofield (1976)

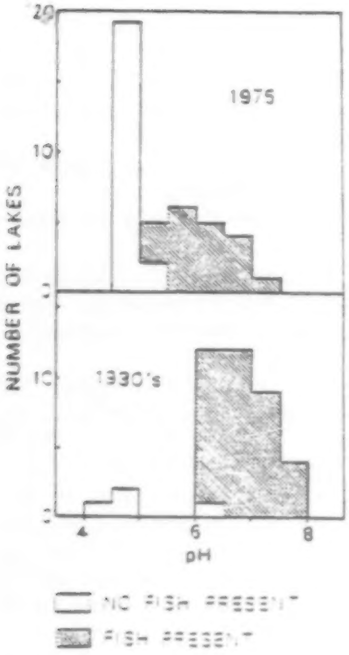

Figure 26. Frequency distribution of pH and fish population status for 40 high elevation lakes surveyed in the 1930s and again in 1975 (Schofield, 1976).

More data on inland fisheries resource impacts from acidic deposition are available from Ontario than from any other province in Canada. The case study of lakes in the LaCloche Mountain range, by Beamish and Harvey, (1972) is best known. These lakes have a naturally low buffering capacity, but are only 65 km southwest of the Sudbury area smelters.

Some of the lakes appear to have already lost fish populations at the time of the first survey, others had populations that were endangered, and still others were apparently in a healthy condition (Beamish, 1976). The fish community of Lumsden Lake (one of 68 examined) has been studied for 14 years. The following chronology of fisheries losses has been assembled by Harvey, (1979), from Provincial Government capture records dating to the early 1960's, and observations by local anglers and residents for some species prior to 1960.

- in the 1950's, 8 species were present
- 1960 last report of yellow perch and burbot
- 1960-65 sport fishery fails (pH 6.8 in September of 1961)
- 1967 last capture of lake trout and slimy sculpin
- 1968 white sucker suddenly rare
- 1969 last capture of trout perch, lake herring and white sucker
- 1970 one fish species present
- 1971 lake chub very rare (pH 4.4 in August of 1971).

This record shows that species vary in their susceptibility to declining pH, but, as outlined previously, the mechanisms by which individual species are eliminated are complex.

The Haliburton-Muskoka area of south central Ontario is one of the most important recreational areas in the province, partly due to the fishing opportunities it provides. Dillon et al., (1978) report that one of the lakes in this area has lost 40-75 per cent of its acid neutralizing ability in a decade or less, and Scheider et al., (1978) conclude that part of the loss is due to acidic precipitation. Projections, based mostly on precipitation chemistry and bedrock geology, have suggested that thousands of lakes in Ontario are potentially susceptible to acidification, if inputs continue at present-day rates.

Quebec, like Ontario, has large numbers of lakes which are potentially sensitive to acid inputs. The scenario for its fishery resource may be similar to Ontario's, but, unfortunately fisheries data that might substantiate this view are lacking.

Impacts on Atlantic salmon: In North America, the Atlantic salmon ranges from Ungava Bay, in the north, to Passamaquoddy Bay, on the Canada-U.S. border, and south in the U.S. to the Connecticut River. Over most of its range, the acidity of precipitation is presently about 10 times greater than "normal" for clean air. Surface water data, currently available from this area, indicate that only in some Nova

Scotia rivers have pH levels fallen low enough to threaten salmonid reproduction.

Within Nova Scotia, the distribution of acid water is well correlated with geology (Watt, 1980). Seasonal variation in the pH of acidified rivers is about 0.5 unit, with the annual minimum occurring in mid-winter, and a maximum in late summer. Historical data indicate that the local rate of acidification has been of the order of 0.3-0.4 pH units in 20 years. At present there are 9 rivers with pH 4.7 which previously had salmon but now have no salmon or trout reproduction; 11 rivers are in the pH range 4.7-5.0, where some juvenile salmon mortality is probably occurring; and 7 rivers are in the pH range 5.1-5.3, which is considered borderline for Atlantic salmon. The acidification threat to these 27 rivers represents only 2 per cent of the total Canadian habitat potential for Atlantic salmon, but in Nova Scotia it represents 30 per cent of the available salmon potential.

Fortunately, there are historical water chemistry data on some of these affected rivers (Thomas, 1960) from surveys performed in 1954 and 1955. In the past 25 years, the pH of the Tusket River has decreased from an annual range of 4.9-6.1 to 4.6-4.9; the Roseway from a range of 4.4-6.4 to 4.3-4.5; the Jordan River from about 5.1 to a range of 4.4-4.6; the Medway River from a range of 5.5-6.5 to 5.1-5.8; and the Clyde River has decreased from 5.0 to 4.6. Alkalinity was not detectable in the Tusket, Clyde, Roseway and Jordan rivers in 1979-80, but was measurable during Thomas' study 25 years earlier. Although Thomas, (1960) sampled some of these rivers only once, his water quality data suggest that salmon reproduction in a few rivers may have been adversely affected due to acidity by the early 1950s. Even to the casual observer, some of the affected streams are strikingly different in appearance from streams with mean annual pH's above 5.0. When they were recently surveyed, in the latter part of the summer, affected stream bottoms were covered with dense mats of filamentous algae, and sphagnum moss had invaded the stream channel in some areas (R.H. Peterson, personal communication).

One of the Nova Scotia rivers "threatened" by increased inputs of acidic precipitation, the Mersey, contains an Atlantic salmon hatchery. The Mersey watershed has poorly developed soils, and its underlying geology is Devonian granite. The mean total alkalinity of samples collected from the river in 1978-79 was always less than 0.5 μg/l, while mean pH was 5.2, with a range of 4.9-5.4. In 1954-56 the river had a mean pH of 5.8, with a range of 5.4-6.6, and a mean total alkalinity of 2.4, with a range from 1.0-4.4 (Thomas, 1960). Mean sulphate values have been estimated to have increased from 1.6 μg/l in 1954-55 to 3.3 μg/l in 1978-79. These data suggest that the river is sensitive to, and has been affected by, atmospheric inputs.

During the period 1975-78, mortality of Atlantic salmon parr, reared at the Mersey hatchery, typically occurred during the 3rd and 4th weeks after first feeding. This higher than expected mortality was attributed to increased acidity in spring river water supplying the hatchery.

In 1979, by treating the water with $CaCO_3$, the salmon fry mortality was reduced from 30 per cent to 3 per cent (Farmer et al., 1980). In 1980 the water was again treated and produced the same dramatic increase in survival of parr.

Some direct field observations of the water chemistry of salmon streams in Newfoundland have been made, but the data are sparse. One stream was found to have a pH of 4.3 in the spring, after a prolonged rain. Electro-fishing revealed 2 adult salmon, but no juveniles. One cannot conclude with certainty that reproduction is being affected, but the lack of data suggests that additional field observations are warranted in those areas of Newfoundland which are potentially sensitive to acidic inputs.

If current acid loadings continue, it appears probable that more of the inland and Atlantic salmon fisheries in Canada will be lost. Portions of Canada's fishery resource appear to be heading in the same direction as the fish stocks in Norway and Sweden. Hendrey and Wright, (1976) report that "acid precipitation has devastated the salmonid fish in southern Norway." Massive fish kills of adult salmon and trout have been reported in their river systems, and usually occur during the spring snowmelt, or after heavy autumn rains. An intensive survey of 50 lakes in southern Sweden showed that inland freshwater species are also threatened. The decreases have resulted in the elimination of Atlantic salmon from many Norwegian rivers in the past 20 years. Scandinavian scientists have concluded that, directly or indirectly, the principal cause of the fish losses is the acidification of the waters, due to acid precipitation.

Potential for Fisheries Impacts in Western North America

Parts of British Columbia, Washington, Oregon and California are potentially sensitive to acidification if acid loadings are increased (Figure 4). There are no data at present from the Region which indicate that the fisheries resources are now affected. Parts of the Prairie Provinces are located on the acid sensitive Precambrian Shield Region. Some lakes in Saskatchewan are downwind from known sources at Cold Lake and Fort McMurray petro chemical processing plants. No data are available at present which indicate that these areas have been affected.

Loss of Genetically Unique Fish Stock

Loss of fish from lakes and rivers appears to be an irreversible process. Over several thousand generations, most species appear to have evolved discrete stocks adapted to similar, yet discrete and specific, habitats (Loftus, 1976). The basic unit of a stock is the gene pool, which is composed of a naturally sustained, genetically variable group of individuals, adapted through evolution to the local environmental conditions. Man-induced stresses (i.e. cultural eutrophication, habitat destruction, over-exploitation, species introduction and contaminants) have, separately and synergistically, reduced this genetic variability in populations of native fishes. Surface water acidification is an example of such a stress. Beamish and Harvey, (1972) documented the loss of gene pools of fish in acidified lakes in Ontario. The Ontario Ministry of Natural Resources has attributed the extinction of lake trout (Salvelinus namaycush) in 27 lakes in the Sudbury-Temagami area to acidification (C. Olver, personal communication).

As the extinction of species has increased with the tempo of human activities, it is likely that the rate of loss of genetically discrete, locally adapted stocks has been many times greater. A naturally evolved complex of stocks appears essential to fully utilize the productive capacity of waters. Therefore, it is important to recognize and preserve stocks (Loftus, 1976). Fisheries managers are now using the stock concept to allocate harvest and rehabilitate fish populations (Ricker, 1972). Continued loss of discrete stocks may inhibit effective re-establishment of naturally reproducing populations in waters undergoing rehabilitation. The ramifications of these losses affect fisheries management, specifically, and society, in general. Genetic variability is a biological resource that must be managed (Ryman and Stahl, 1981) or future opportunities for economic and recreational use of this resource will be jeopardized.

Effects of Acid Precipitation on Birds and Mammals

Only four reports have attempted to relate acidification to changes in avian or mammalian populations. In a review paper, Almer et al., (1978) reported that, "fish-eating birds, such as mergansers and loons, have been forced to migrate from several acid lakes, with decreasing fish stocks, to new lakes with ample food supply. In this way, many territories will become vacant, and this will lead to decreasing stocks." The extent of the problem in Sweden has not been documented at this time. In another Swedish study, Nilsson and Nilsson, (1978) found a positive correlation between pH and "water" bird species richness. "Water" birds were defined as those species dependent upon open water, and included a loon species, and several waterfowl and gull species. Nilsson and Nilsson, (1978) suggested that a reduction in young fish, a very important food source for aquatic birds, may lead to low reproductive success and local extinction in some bird species.

In North America, the only information on changes in aquatic bird populations comes from New York's Adirondack Mountains and relates to the Common Loon (Gavia immer). Loon nesting densities have declined over the past 15 years (McIntyre and Manas, 1979; Trivelpiece et al., 1979), during which time fish populations in this area have also declined (Schofield, 1976). To date, however, changes in loon populations in this area have only been interpreted with respect to human disturbance, and the probable role of food depletion has not been adequately investigated.

The loss of food organisms in acidic lakes gives rise to potential effects on wildlife dependent upon the aquatic system, and includes three groups, based on feeding habits - piscivores, other carnivores and omnivores, for which animal food comprises an essential part of the diet during breeding. Effects due to changes in vegetation have not been considered, due to the lack of information. Table 3-11 is a summary of potential effects on selected species of birds and mammals dependent upon the aquatic ecosystem for their food and habitat.

Effects on Unique Ecosystems Including Rare and Endangered Species

Documentation of acid precipitation effects on unique ecosystems and rare and endangered species is sparse at the present time. Negative effects on rare species will result in a decreased gene pool diversity. Aesthetic values of these ecosystems may be affected by changes in species composition. Many of these sites are presently National Parks or National Forests in both the U.S. and Canada, and protected by federal laws. Placing an economic value on such ecosystems (and species) is difficult, but their value to society is immense. The following paragraphs briefly summarize existing information on potential acid precipitation effects on these systems.

The Boundary Waters Canoe Area Wilderness (BWCAW) of northern Minnesota has been recognized as a unique resource for many decades, as evidenced by the various laws passed since 1930 to protect its wilderness state. The attraction of the area (it attracts more recreationists than any other wilderness area in the nation) does not appear to be based on any single factor, but on a combination of related ones, such as fishing and camping in an atmosphere of wild, unpolluted landscape. However, the evergreen forests, clear water and air, rock outcrops, and shallow soils which are the conspicuous ingredients of the BWCAW landscape, are all unusually sensitive to regionally transported pollutants. Small additions of acidity to the thin, rocky soils common in the BWCAW, coupled with geochemical weathering, can be expected to have relatively rapid and irreversible effects on outputs from the nutrient cycles of these ecosystems (Glass and Loucks, 1980). These changes will affect groundwater quality, and produce soil-mediated changes in cycling rates within the ecosystem.

The BWCAW is in a region comparable in vulnerability to others in Europe and North America which have already been severely affected by acid precipitation. Most surface waters have a poor buffering capacity, and many have a low pH (below 6.5) as well. The varied and valuable fisheries resource includes many species that have been reduced, or eliminated, by acid precipitation elsewhere in the United States and Canada. Atmospheric acid sulphate loadings near the BWCAW are at levels associated with the onset of lake acidification in Scandinavian countries. Because of this, it is likely that the most vulnerable lakes are already being affected by acidity from atmospheric sources (Glass and Loucks, 1980).

TABLE 3-11

AVIAN AND MAMMALIAN SPECIES
SUSCEPTIBLE TO THE EFFECTS OF ACID PRECIPITATION

Susceptible Food Resources	Requirement for Food Resources	Species
Fish, amphibians, aquatic invertebrates	Primary food of adult and young	Common loon (Gavia immer)
		Common merganser (Mergus merganser)
		Hooded merganser (Mergus cucullatus
		Red-breasted merganser (Mergus serrator)
		Great blue heron (Ardea herodias)
		Belted kingfisher (Megaceryle alcyon)
Aquatic invertebrates, small fish	Primary food of adults and young	Common goldeneye (Bucephalus clangula)
Aquatic invertebrates	Food of adults and dominant food of downy young	Ring-necked duck (Aythya collaris)
Aquatic invertebrates	Primary food of laying hen and downy young	Black duck (Anas rubripes)
		Green-winged teal (Anas carolinensis)
		Mallard (Anas platyrhynchos)
		Northern pintail (Anas acuta)
		American widgeon (Anas americana)
Fish, amphibians, aquatic invertebrates	Wetlands	American mink (Mustela vison)
		River otter (Lontra canadensis)
Aquatic invertebrates, amphibians	Wetlands	Muskrat (Ondatra zibethicus)

After Clark and Fischer, (in preparation)

The Kejimkujik National Park in Nova Scotia lies in an area considered to be highly sensitive to acidic inputs, because it is composed of shallow, impoverished soils on primarily granitic and quartzite bedrock. Boulder-strewn bedrock plains and poorly drained soils are common. The effects on the salmon of this area have already been reported. Much of this region is dominated by what is referred to as a "Southwestern Flora" (Roland, 1944), and contains a total of 75 plant species which occur either only in this area and in southern New England, or locally in other parts of eastern Canada. They are, however, more abundant in this part of Nova Scotia. The effects of acid precipitation on terrestrial ecosystems in Nova Scotia have not been documented, and the tolerance of the indigenous rare plants to elevated aluminum concentrations is unknown. Acid precipitation effects on Nova Scotian rivers are well documented, and were reviewed previously.

A third unique wilderness area, considered sensitive to acidic inputs, is the high elevation system of the Adirondack Mountains. These areas consist of shallow, poorly buffered soils and, on the mountain tops, contain many arctic species that are rarely found in the eastern United States. Acid precipitation is known to be affecting the fish species of lakes in these areas (Baker and Schofield, 1980), but effects on terrestrial organisms are less well documented. It is of particular importance to determine the tolerance of these unique species to elevated aluminum concentrations.

Effects of acid precipitation on fish populations of the Great Smokey Mountains National Park (GSMNP) have been reported by Hermann and Baron, (1980). Elevated aluminum concentrations (>1.0 mg/l) have been shown for GSMNP streams, with the apparent adverse effects of these concentrations on brook trout populations. The high aluminum concentrations occur in association with acid runoff as low as pH 4.1. No studies have yet discussed the impacts of elevated aluminum concentrations on rare and endangered plant species (and other more common species) found in the southern Appalachian area, including the GSMNP.

CONSIDERATION OF EVIDENCE FOR IRREVERSIBLE IMPACTS

Researchers differ, and the evidence seems to be conflicting, as to whether the geochemical alteration of watersheds, due to acidic inputs, should be viewed as irreversible, and, if so, on what scale. Irreversibility can be viewed as a failure to recover over geological time; but, for natural resource systems, an incomplete recovery to a prestressed or undamaged state over a few decades, for all practical purposes, may be regarded as irreversible. The following sections summarize the concepts involved and the evidence on both sides of the question.

Depletion of Buffering Capacity

The possibility of irreversible loss of buffering capacity in lakes and watersheds is one of the most serious potential impacts of acid deposition. Once the proton accepting materials, which hold pH in a biologically acceptable range, are lost from the soil water and stream base-flow, free H^+ or its surrogate, Al^{3+}, rise quickly to toxic levels, seriously weakening the biota. The pH of an aquatic system is a product of a dynamic equilibrium between the system and its watershed. Acidic deposition has the potential to modify this equilibrium in geologically sensitive watersheds, and certain data suggests it has done so in a few areas.

The ability of lake water to resist pH depression, when acid is added, (i.e., buffering capacity), depends on its alkalinity. The alkalinity of the water depends on the presence of anions, or other species, which can take up protons. In most natural waters, alkalinity is largely a function of bicarbonate, but other substances, such as organic acids, silicates and ammonia, are important in the low alkalinity lakes most susceptible to acidification. When lake water is titrated with acid, the change in pH per unit of added acid (i.e. the slope) varies as successive buffers are protonated, each acceptor taking up protons in its own characteristic way. Lakes of moderate pH show successive buffering in the titration curves shown in Figure 27. In a whole lake system, this process is further complicated by the variable mixing processes in the lake, and the spatial and temporal changes in biological productivity, which also contributes proton uptake capacity (Zimmerman and Harvey, 1979).

When titration is considered for an entire watershed, as may be the case from sustained long-term atmospheric acid inputs, the same buffering processes can occur. However, the reaction is much more heterogeneous in a watershed, and the total quantity and variety of proton acceptors is probably greater. Contact between protons in water and the solid buffering materials in the soil is not assured, depending on hydrologic flow patterns within both the upper ("inter-flow") and deeper soil horizons. Periods of peak runoff, when much of the "surface" water penetrates only a few centimeters into the soil, are often associated with acid flushing (low pH), apparently with little buffering. This process is more likely to occur when watershed buffering is naturally low or may have been depleted by long-term acid input. In addition, inclusion of the soil system in the buffering reactions introduces new sources of buffering which can retard pH depression in the system, but lead to the mobilization of cation nutrients and toxic materials. When soil pH is less than 5.0, the displacement of aluminum from exchange sites becomes a major source of buffering (where it is present); however, in the process, aluminum takes on a soluble, often toxic, form, with risks for both terrestrial and aquatic biota.

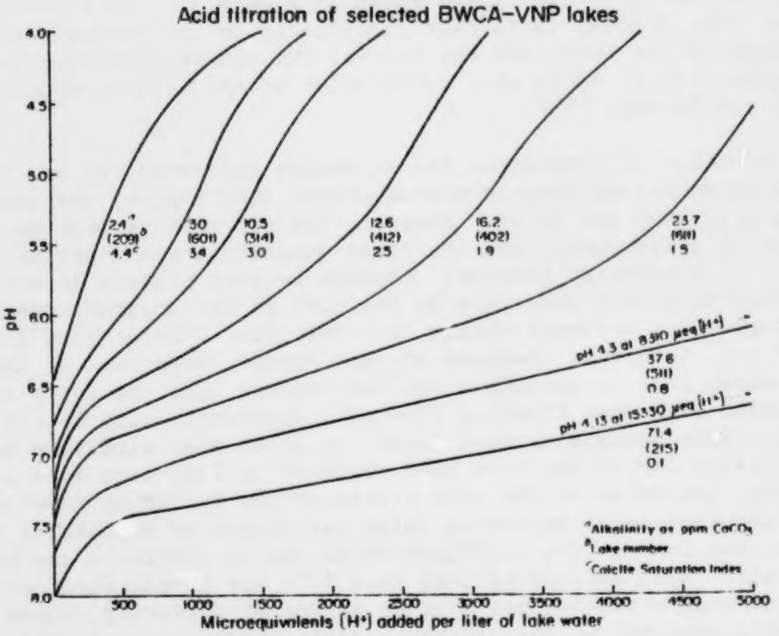

Figure 27. Effect of acid addition on the pH of water from selected BWCAW-VNP lakes (Glass and Loucks, 1980).

The hypothesis that acidification of surface waters by atmospheric acid inputs can be viewed as a large scale titration has been articulated by Henriksen, (1980), and supported with data from North America and Scandinavia (Wright et al., 1980). Nearly all lakes, except those dominated by acid bog drainage water, are normally bicarbonate buffered, with pH greater than 6.5. By stoichiometry, addition of acid from the atmosphere will consume alkalinity, but the pH will fall only slightly, as long as some bicarbonate remains. Long-term (more than 50 years) records of decreasing alkalinity in a water supply reservoir in the Adirondacks suggest that alkalinity has declined with the continued atmospheric acid input (C.L. Schofield, personal communication). As bicarbonate and any other buffers are depleted, Henriksen suggests that lakes enter a transition phase, characterized by severe pH fluctuations (1-2 units), and associated stresses on fish and other aquatic biota. This transition phase is a time when the lake is particularly susceptible to seasonal pulses of acid (e.g. snowmelt), and to the incomplete "mixing" of water and soil during flushing events. According to this view, a lake may exist in a transition phase until the last carbonate or other buffers in the watershed are consumed. However, given the continued acid input, this stage is relatively ephemeral.

In another study, Wiltshire and Machell, (1980) found that surface water pH values in Nova Scotia have a bimodal pH distribution, with the fewest lakes at pH 5.5, approximately in the middle of Henriksen's "transition phase". Scandinavian data also support these results (Wright and Gjessing, 1976). If watershed titration is occurring, then ultimately, when H^+ is added to deplete the bicarbonate alkalinity, the lake pH should approach 5.0, where buffering occurs by aluminum, organic compounds and other proton acceptors. Although one cannot be certain, these appear to be the responses being observed, and it is at this stage that fish and other biota become severely depleted or absent.

The hypothesis that a relatively irreversible titration of the chemical components of a watershed contributing to the buffering capacity can take place is a simplification of the complexities of lake/watershed buffering discussed in previous sections. The variety of potential sources of buffering, water flow patterns and rates of acid deposition and flushing, all tend to make each lake/watershed system unique. However, the general pattern of observed responses is consistent with the known low buffering capacity of the geology and soils, and with present equilibrium theory for these systems. The effects can only be reversed by regeneration of buffering capacity over a period of unstressed geological weathering. The transition phase of lake acidification appears to be the last chance to halt acidification and allow normal acid-base equilibria to be established, with H^+ and Al^{3+} in a biologically tolerable range.

Soil Cation and Nutrient Depletion

A second, apparently irreversible, consequence of watershed titration is the loss of soil cations, particularly Ca^{2+} and Mg^{2+}, which can lead to decreases in soil fertility. Likens et al., (1977) summarized the watershed level dynamics of a variety of anions and cations over an 11-year period at Hubbard Brook. During this time there were net outputs of Ca^{2+}, Mg^{2+}, K^{+}, Na^{+} and Al^{3+} at a combined rate that exceeded the rate of H^{+} deposition. The difference was attributed to internal sources of H^{+}, although equilibrium theory suggests that smaller net losses of these cations would be accounted for by internal sources of H^{+} and external sources of anions prior to the acidification of rainfall inputs. In the 1964-1974 period, virtually all of the H^{+} deposited from the atmosphere was taken up by the system, in exchange for the above cations.

Similar results are reported by Dillon and Kramer, (1980), who find cation denudation at a variety of watersheds in North America and Scandinavia. They try to distinguish the various processes accounting for the weathering and cation export, and find that the sum of the H^{+} input, bicarbonate output and NH_4^{+} input usually balances the sum of the output of metal cations and nitrate input. H^{+} and NH_4^{+} are obvious sources of hydrogen ion for exchange, and HCO_3^{-} output is a measure of carbonic acid weathering. Nitrate has the effect of neutralizing H^{+} by generating an OH^{-} when it is taken up in the nitrogen cycle. If H^{+}, NH_4^{+} and HCO_3^{-} in the watershed do not balance metal cations and nitrate, organic compounds are suggested as the weathering agents.

If cation denudation depletes the stock of nutrients on the exchange capacity of easily weathered soil, fertility decreases can result. These responses should be tied to the process of watershed titration, but the connections are unclear at this time. More data are necessary on rates of chemical transformation in the soils, and the relative role of acid deposition, nutrient dynamics and the nutritional requirements of the plant community.

Loss of Gene Pools (Unique Ecosystem Components)

The most serious irreversible biological effect of acidic deposition is species extinction within sensitive regions. The species most threatened include amphibians, fish, crustaceans, molluscs and some aquatic insects (see previous sections). Elimination of fish populations in numerous water bodies has already occurred in Scandinavia, the Adirondacks and parts of Ontario. For these sensitive organisms, even a partial loss of populations bearing genetic characteristics intolerant to H^{+}, Al^{3+}, or heavy metals, can result in a relatively permanent mark on these populations. As geographic movement of these lacustrine life forms is limited, recovery of pre-stressed genetic characteristics probably can be considered only over millenia. The ecological importance of this impact will depend on the possible availability of stocks which might substitute in the impacted areas.

Other Irreversible Effects Not Yet Fully Defined

Several poorly-known components of ecosystem functioning also seem likely to remain in a modified state from acidic inputs, particularly nutrient and material cycles. Decomposition of organic matter can be retarded by acid conditions as bacterial populations are replaced by fungi. These reactions affect the nitrogen cycle, including nitrogen fixation, and ultimately change the organic matter of acid forest humus layers.

ASSESSMENT OF THE SIGNIFICANCE OF ANNUAL SEASONAL AND EPISODIC ATMOSPHERIC POLLUTANT LOADINGS

SIGNIFICANCE OF LOADINGS AND EPISODES IN THE HYDROLOGIC CYCLE AND POLLUTANT EFFECTS

Seasonal and Short-Term Characteristics of Rain, Snow, Snowmelt and Pollutant Effects

The evidence, in previous sections of chemical and biological alteration of surface water systems, has shown pH depression and associated effects in relation to annual, seasonal and event-related variation in inputs. This section will consider the significance of these levels of chemical alterations, with emphasis on the levels of atmospheric input which can be viewed as having "no effect" on the most sensitive headwater streams and lakes. Evaluation of a "no effect loading threshold", or "sustainable" loading rate, which may yield moderate, but "acceptable effects", requires consideration not only of mean pH trends, but also of the frequency and severity of brief periods during which much of the response to the loading dose may be expressed.

The following are the principal findings presented in previous sections, which bear on the interpretation of the significance of pollutant loadings:

Physical Response System

Pollutant deposition processes are inherently episodic, and the concentrations of chemicals in rain water and surface waters have event-related properties similar to those of hydrographs and air pollutant concentrations.

Fluctuations in atmospheric circulation patterns and precipitation, over periods of one to several years alter deposition amounts and concentrations, thus creating periods of years when acidification is greater or less than long-term averages.

Certain chemical reactions in soils, soil-water and aquatic systems (e.g. mobilization of some metals) occur only when H^+ concentrations have reached critical levels, as, for example, during snow melt, post-drought rains, or other flushing events.

Exposure of organisms to toxic ions, other than H^+, appears to occur primarily during short periods of elevated H^+ concentrations, and these may be estimated very poorly by annual average, mid-summer or even any in-lake measurements of pH.

Biological Response System

Laboratory studies have shown that the sensitivity of most organisms to H^+ and other chemicals in the aquatic environment varies with life stage, from fertilization of eggs, through hatching and survival of young, to adulthood.

Whether the most sensitive life stages occur in conjunction with the seasonally elevated H^+ is predictable for some species (i.e. spring-spawning fish and amphibians), and serendipitous for other species (responding to mid-summer or fall acid-flushing events).

Evaluation of a "no effect" threshold or an "acceptable effects" threshold will have to take into consideration a probability distribution for the conjunction of sensitive life stages with unusual acid-flushing events which may have a periodicity of once per decade.

DEFINITION OF LOADING THRESHOLDS FOR AQUATIC RESOURCE IMPACTS

As discussed elsewhere in this report, the acidity and chemical make-up of waters of aquatic ecosystems are controlled by two factors: the buffering capacity of the geologic components of the basin, and the effective acidity of the precipitation. Fully validated deterministic models of the acidification of the aquatic regime are not available at this time, and their development and application will require detailed information on basin geochemistry which is unlikely to be available soon for widespread application. It is, therefore, possible to relate the permissible carrying capacity of basins to acidic loadings in only a general way, at present. The models now available use the presently observed behaviour of stream and lake systems to derive relationships between parameters of acid loading and system response. These models are all under active development, but have advanced to the point where a preliminary application is possible, although it is important to stress that full validation remains to be achieved. Several of these models are discussed below, in order to evaluate relationships between loading thresholds and lake or stream sensitivity, as they are reflected in each approach.

Dickson Relationship

One way to summarize the relationship between lake pH and atmospheric loading and acidic pollutants is the plot of lake pH over sulphate loading, summarized by Dickson (Almer et al., 1978) (Figure 28). Various combinations of watershed characteristics are reflected in the family of curves connecting the different sets of lake data. A larger

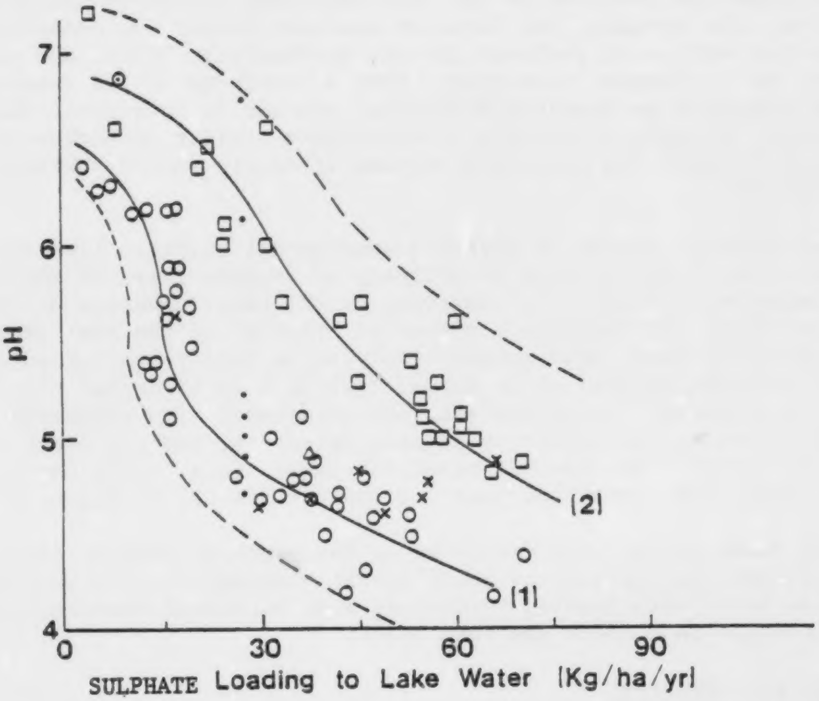

Figure 28. Effects of various sulphate loading rates on lake pH for lakes in very sensitive (1) and somewhat less sensitive (2) surroundings in Sweden. Added points are for: (•) Florida (Crisman and Brezonik, 1980); (⊙) Como Creek (Lewis and Grant, 1979); (Δ) Hubbard Brook (Likens et al., 1977); and (x) Norway (Wright and Snekvik, 1978). (modified from Almer et al., 1978).

number of curves may be envisioned, each representing lake/watershed systems of comparable sensitivities, as they apparently respond to increases in atmospheric acid inputs. The curves are superficially similar to titration curves, as might be expected, and each shows buffering at high pH, then a rapid drop (as this buffering apparently is depleted) to lakes with low pH and minimal buffering. The pH in the more sensitive lakes drops sooner and more rapidly, relative to the loading of SO_4^{2-}.

A graph of sulphate deposition versus lake pH could be used to determine lake/watershed sensitivity, and therefore acid loading tolerance, by evaluating the position of the lake/watershed system on the response curves. For example, the lakes of southern Norway are underlain by granites and felsic gneisses (Wright and Snekvik, 1978), and almost all prove to be somewhat sensitive. From a knowledge of the response of very sensitive geochemical/biological systems in moderately impacted systems, it appears possible to anticipate similar responses in the future on similarly sensitive systems if acidic inputs increase or are sustained.

Examination of Figure 28 suggests that annual sulphate loadings of less than 15 to 17 kg/ha would be unlikely to degrade lakes of the type represented in curve (1). However, if the lower envelope of the data distribution is viewed as a potential "family" of the most sensitive lakes and streams, they appear likely to be barely free of potential acid loadings effects at an annual rate of 9 to 12 kg/ha/ yr. Thus, two "tolerances" can be defined, one associated with projected protection of nearly all sensitive aquatic resources, and the other with protection of less than all sensitive lakes, (e.g. only the half of the "sensitive" resources that lie above curve (1) in Figure 28).

Since these curves were developed on the basis of Swedish data, and are not actual observations of acidification responses over time, these estimates of acid loading tolerances must be viewed very cautiously for application in a North American context.

Henriksen Nomograph

Henriksen, (1980) presents a model based on the concepts implicit in titration of a bicarbonate-buffered lake with strong acid (principally H_2SO_4) from the atmosphere. In the process, bicarbonate is depleted, and lake pH can fall below 5, with consequent effects on aluminum mobilization and fish. These relations are basically the same as those in the Dickson work, and are summarized in the nomograph (Figure 29), using two key measurements:

1. ambient concentrations of in-lake calcium (or Ca + Mg), as an estimator of the pre-acidification alkalinity; and

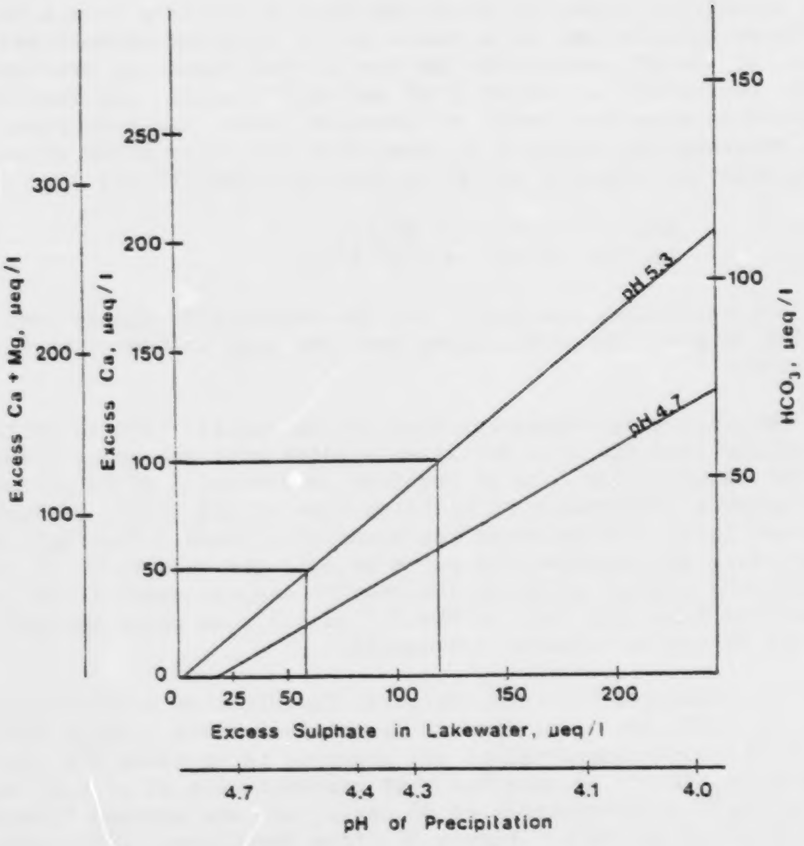

Figure 29. Nomograph to predict the pH of lakes given the sum of non-marine calcium and magnesium concentrations (or non-marine calcium concentration only) and the non-marine sulphate concentration in lake water (or the weighted-average hydrogen ion concentration in precipitation) (Henriksen, 1980).

2. lake sulphate concentrations (in excess of marine input), as an estimator of H^+ added to the system.

The resulting semi-predictive nomograph is divided into three sections:

1. bicarbonate lakes, where original alkalinity was high and/or added H^+ is low, so that the lakes remain bicarbonate buffered;
2. acid lakes, where original alkalinity was low relative to acid inputs, and all bicarbonate appears to have been depleted by the acid addition; and
3. transition lakes, in which bicarbonate appears to be undergoing reduction (or is almost depleted) and large pH fluctuations occur during runoff events.

The transition phase, in which the lake is shifting from a bicarbonate buffered equilibrium, at moderate pH, to an aluminum-buffered equilibrium, at low pH, represents the key process requiring prediction. This shift apparently is forced by H^+ and SO_4^{2-} inputs, and Henriksen presents regression equations based on Norwegian lakes, and precipitation data for representing sulphate in lake water (SO_4*) in terms of sulphate in precipitation [$SO_4(p)$] and H^+ in precipitation [$H^+(p)$]:

$$SO_4^* = -19 + 1.9\ SO_4(p)$$
$$SO_4^-(p) = -2.7 + 1.37\ H^+(p)$$

All concentrations are µeg/l, and the sulphate is excess over that from marine origin. These equations have not been validated to North America.

The methodological component that can be applied here to estimate threshold loadings from Henriksen's model must use input assumptions as to the steady state lake pH required to protect a given percentage of the aquatic resources. Maintaining a pH of 5.3 would, presumably, prevent lakes from entering the transition phase. This method, however, does not consider the pulse or episodic occurrence of low pH during the spring, although the results suggest these lakes would be protected from acid rain in the 5.3 to 4.7 zone where episodic events of low pH can be expected frequently.

The U.S./Canadian Bilateral Research Consultation Group (Altshuller and McBean, 1980) has classified as "sensitive" those aquatic systems in which calcium concentrations are observed to be below 200 µeq/l. From Figure 29, it can be observed that precipitation pH of 4.5, and lakewater SO_4^{2-} concentrations of 60 µeq/l, are the maximum tolerable for waters of 50 µeq Ca/l. Figure 30 (from Henriksen, 1979) shows the numbers of lakes in Norway having Ca values in the 0 to 50 and 50 to 200 µeq/l range. Using Henriksen's relationship of lakewater excess SO_4^{2-} to precipitation SO_4^{2-}, this in-lake concentration of SO_4^{2-} converts to a precipitation SO_4^{2-} concentration of about 40 µeq/l. The nomograph indicates that successful abatement of SO_4^{2-} to this level

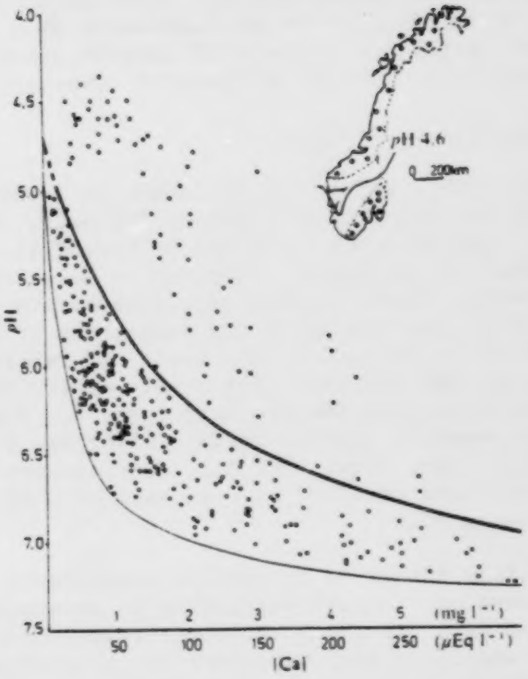

Figure 30. pH and calcium concentration in lakes in northern and northwestern Norway sampled as part of the regional survey of 1975, in lakes in northwestern Norway sampled in 1977 (o), and in lakes in southernmost and southeastern Norway sampled in 1974 (●). Southern Norway receives highly acid precipitation (pH 4.2-4.5) and a large number of lakes have lost their fish populations due to high acidity. Inset shows areas in which these lakes are located. Areas south of isoline receive precipitation more acid than pH 4.6. (Henriksen, 1979).

would protect lakes having present calcium concentrations of 50 μeq/l, or more.

Apparently, even lower SO_4^{2-} concentrations in precipitation would be required to protect lakes with calcium levels below 50 μeq/l. To protect lakes with only 25 μeq/l of calcium from prospective acidification (the entry level to transition phase) would require precipitation with no more than 25 μeq/l of sulphate rainfall (pH 4.7).

It is important to realize the limitations of the hypothesis employed to derive these estimates. The contributions of NO_x or NH_4^+ to the acidification are not considered, nor are possible variations in basic cation concentrations in precipitation. (The latter tend to raise the measured values of rainfall above the calculated pH.) Thus, a more comprehensive and verifiable estimate of aquatic acidification carrying capacity must await the findings of research presently being conducted.

Cation Denudation Rate (CDR) Model

Work by Thompson, (1980) and others in Canada is leading to comparative studies of cation depletion in watersheds, following varying rates of acid deposition. Alternatively, CDR can be viewed as the proton absorptive capacity (PAC) of the basin. Thompson et al., (1980) report that the Tusket and Medway Rivers in Nova Scotia have PACs of about 80 meq/m^2/yr. In 1973, when the pH of the Tusket was little higher, if at all, than the pH of precipitation, its basin had received an acid load equal to or greater than its PAC. The Medway River, further east, probably received a somewhat smaller acid load, but its mean pH, 4.88, is also low. The basin of the St. Mary's River has a larger PAC, about 115 meq/m^2/yr, and, because of its location even further to the northeast, may well have received an even smaller acid load, yet its mean pH was as low as 5.16.

The question is often raised as to whether atmospheric loads of strong acid alter the rates of chemical weathering in watersheds, and therefore the PAC. The data for the Nova Scotia rivers indicate that such changes are very small, if any, but there may be a slightly reduced rate of cation denudation (or proton absorption capacity) with time, as shown in Figure 31. The reasons for such a decrease are only speculative at present, and may be related to such subtle processes as a reduced rate of forest growth and root development. It is to be hoped that the calibrated watershed studies, now being carried out in various parts of eastern Canada, will answer such questions.

For reasons of potential consistency with the known watershed response processes, the evaluation of a loading tolerance based on "proton absorptive capacity" has many advantages. To date, however, only indirect evidence can be used to estimate (by this method) the loading capacity for elevated proton additions in watersheds.

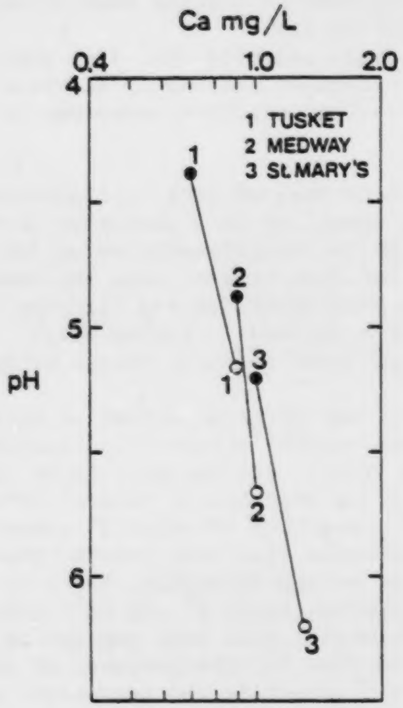

Figure 31. Log Ca^{++} versus pH for the three Nova Scotia Rivers, 1954-1955 (●) and 1973 (o) (Thompson et al., 1980).

Further research, using the developed watershed data bases, may provide a strongly based methodology in the next few years.

Episodic Receptor Dose/Response Relationships

The data presented in previous sections have established three relationships with a high degree of probability:

1. Stream chemical responses show a time-trend over two to five decades, during which pH and alkalinity declines have been more or less continous.
2. The populations of sensitive fisheries (e.g. salmon, white sucker and other) have declined in streams when pH values have declined to annual means of 5.2 to 5.5.
3. Physiological evidence suggests that fish population effects are due to acute short-term or seasonally elevated H^+ and Al^{3+} ions, known to produce serious negative responses in fish at certain life stages.

Measurements of lake or stream pH tend to fluctuate considerably during the year, and average annual pH is a composite of these patterns. Thus, summertime or annual pH has questionable value for physiologically-based organism responses. For this reason, plus the known significance of brief acute exposures, the magnitude and duration of short-term increases in H^+, associated with a defined "flushing event", may be a useful model for defining a critical dose/ response relationship.

Research on brook trout and Atlantic salmon by Daye and Garside, (1975, 1977, 1980a, 1980b) and related research by Beamish and Harvey, (1972), Beamish, (1974a,1974b, 1976), and Harvey, (1975, 1979, 1980) have provided a broad understanding of the response of several pH-sensitive fish species to both long-term and short-term elevated H^+ exposures. Mortalities of fish eggs, sac-fry and adult fish have been documented for chronic pH depression, and effects on egg viability, hatching success and adult survival from short-interval acute H^+ and Al^{3+} exposures are reasonably well known. The experimental data base supporting these relationships was cast in generalized form for the purposes of developing a simulation model of H^+ and Al^{3+} flushing and associated effects (Andrews et al., manuscript in preparation).

Among the experimentally-based relationships used in the model is a recurring pattern:

1. the short-term acute exposure of "shock" effect can be expected over a range of as little as 0.5 to 1.5 units of the pH scale;
2. these shock exposures can be thought of as being significant across a range of pH above the level at which background H^+ would produce little effect.

These data show a pH depression (Δ pH) of 0.7 to 1.0 to be a response of substantial physiological significance. This relatively deep depression of pH during shock events is probably to be expected only in regions where acidic deposition has already produced a time-trend downward in stream pH and alkalinity, as shown in several monitoring programme already cited. Even sensitive regions, free of long-term acid inputs (or in the first to second decade of moderate deposition), appear unlikely to experience a short-term pH depression of these magnitudes.

Given this dose/response relationship, a loading threshold can also be defined as the daily (or monthly) H^+ loading (or equivalent SO_4^{2-} acidity) which, when subjected to a defined flushing event (e.g. snow-melt or first major rainfall following drought), leads to the minimal biologically significant short-term H^+ and Al^{3+} exposure.

The data available on pH depression during flushing events indicate a range in responses, from 0.3 to 1.0 pH units of the pH scale during snow-melt in northern Minnesota (Glass, 1980), to about 1.0 unit on the Shaver's Fork River in West Virginia (Dunshie, 1980), to more than 2.0 units observed in the Adirondacks (Galloway et al., 1980). Values in this range have also been reported for Hubbard Brook (Likens et al., 1977), and Plastic Lake, Ontario (Zimmerman and Harvey, 1979). Peak concentrations of Al are often associated with these peak H^+ flushing events.

The maximum pH depression during a flushing event, outside the snow-accumulation regions (i.e. southern United States sites), appears to occur during a major rainfall event (in the order of 1.5" rainfall or more) following a rain-free period (E. Cowling, personal communication; NADP data base; Dunfries, 1980). Thus, a normal "flushing event" can be defined as the response attributable to acidic inputs flushed by the equivalent of a 1 to 2" rainfall or snow-melt into streams of 10 to 500 c.f.s. flow, following a period of accumulation of acidic deposition in snow or surface litter and foliage. Part of this deposition could occur during light rains or from fog condensation.

Figure 32 summarizes the data available on the general relationship between SO_4^{2-} deposition and pH depression (Δ pH) for the flushing events observed. (A "standard" flushing event can be determined from a hydrographic log-distribution of event magnitudes and associated pH depression). The two solid lines have been drawn to be equivalent to the two groupings of lakes studied by Dickson (Figure 28).

The critical receptor response, defined as a pH of 0.7 to 1.0 units, can now be used to interpolate the annual SO_4^{2-} threshold loading associated with that response, in watersheds of a defined sensitivity range, and at a limited range, of dilution and return interval for the episode. Recurrence at an average of once a year, during critical life cycle stages, would be consistent with the physiological studies described above. From Figure 32, a sulphate loading of 5 to 7 kg/ha/yr is seen to produce a critical receptor response (Δ pH in the range of 0.7 to 1.0) for the envelope bounding the most sensitive streams. A loading threshold of 7 kg SO_4^{2-}/ha/yr converts to about 21 μeq SO_4^{2-}/l (assuming 70 cm/yr precipitation), very similar to the value derived from the Henriksen nomograph for protection of lakes having 25 μeq Ca/l or more.

Although the receptor/dose relation incorporates physiological data on organism sensitivity to H^+ (and associated Al^{3+}), further work is required to investigate fully the assumptions and relationships needed for this approach to defining acid loading tolerances. The episodic ΔpH receptor dose/response will need to be cast in terms of streams of a limited range in flow rates (i.e. probably excluding large rivers, since large drainage areas dampen the "shock nature" of the episode), and seasonal rivulets (small intermittent streams, not supporting fish life), and evaluated with respect to interval and deposition accumulation.

Implications of the Models

The models presented above have been largely independently derived from different data, but all contain closely related assumptions. All of the models recognize that significant biological impacts occur in watersheds under stress (i.e. potential transition lakes) and experiencing a physiologically important alteration of water chemistry. The threshold loading tolerance to SO_4^{2-} inputs, which will protect resources of a specified sensitivity can be calculated from each model, within the limits for each method (in each case, still being evaluated).

From application of the above models, one can derive that a sulphate concentration reduction to about 40 μeq/l will result in an increase of precipitation pH from 4.2 to 4.5 in the areas most heavily loaded at present. This precipitation pH may not protect the most sensitive streams and lakes. The estimate of 21 μeq/l SO_4^{2-}/l results in a precipitation pH of about 4.8. Atmospheric modelling should be applied to determine what changes in sulphate concentration will be observed in areas outside of the 4.2 precipitation pH contour. Analysis of precipitation data for North America should lead to revision of these estimates in rainfall pH improvement, including background cation content.

D.W. Schindler, (personal communication) has suggested that precipitation pH probably should be no lower than 4.7, and that it may need to be higher to protect the most sensitive resources. He states:

> "Two studies, one in Scandinavia and one in Canada, have shown that detectable decreases in pH are measureable where precipitation with a pH of 4.7 or less and low alkalinity lakes occur together (Watt et al., 1979; Henriksen, 1980). We know from other works that where precipitation is more acidic than 4.7, aquatic damage occurs rapidly

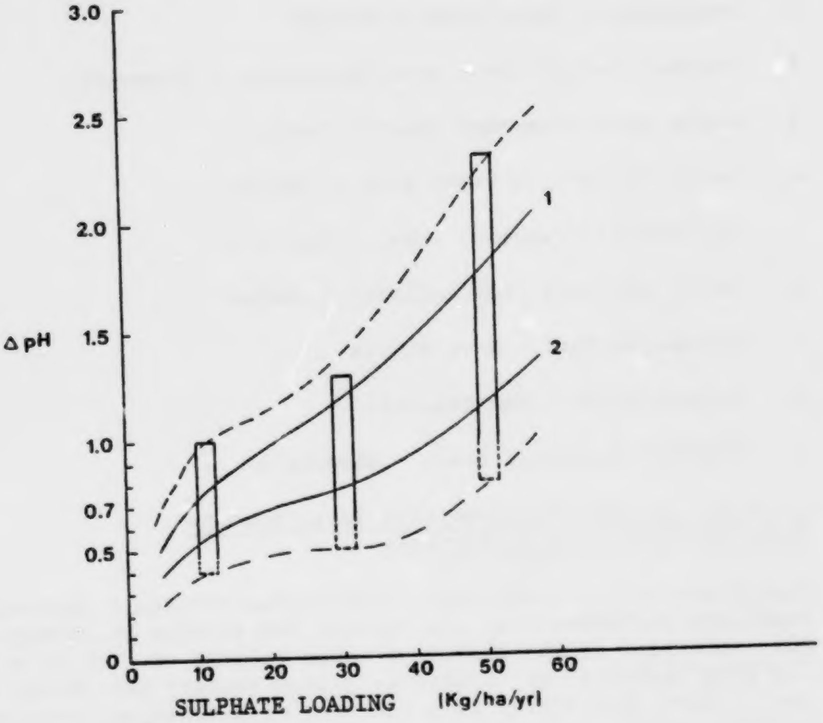

Figure 32. Relationship between atmospheric acid loading (measured as sulphate) and pH depression of surface water for major flushing events in sensitive (1) and somewhat less sensitive (2) areas of North America (Loucks, 1981).

> (Dillion, et al., 1979; Henriksen, op. cit). Studies at the Experimental Lakes Area, Ontario have shown that damage at precipitation pH values of 5.0 is not detectable so far. Preliminary evidence suggests that in sensitive areas, a precipitation pH of no less than 4.7 is desirable."

Reasonable validation of the proposed models will require considerable research, and, owing to the differences in geology and climate, the European models may be not applicable in either the U.S. or Canada. Study areas for evaluating atmospheric transport models and loading predictors should coincide with detailed studies of sensitive receptor areas and areas where specific research measurements can be obtained to permit verification. The areas that should be considered include:

1. Experimental Lakes Area - Ontario
2. Boundary Waters Canoe Area Wilderness - Minnesota
3. Algoma Area Watershed Study - Ontario
4. Dorset-Haliburton Study Area - Ontario
5. Adirondacks (Sagamore Lake) - New York
6. Laurentide Park (Lac Laflame) - Quebec
7. Kejimkujik Park - Nova Scotia
8. Hubbard Brook - New Hamshire
9. Northern Highlands Lakes - Wisconsin

Illustrative Dose/Response/Time Relationships Under Selected Loading Patterns

Regardless of the model used to determine threshold loading values, there are variables that lie outside the purview of effects modelling. Most important is the number of lakes (placed at risk by a given "loading capacity" or "tolerance") that society may choose not to protect. Lake sensitivity is a function of geochemical processes in highly variable lakes and watersheds; abatement to a level that protects the single most sensitive stream or lake in the U.S. or Canada is probably not possible. Once aquatic systems are inventoried, according to sensitivity measures a cutoff point can be determined for various loading tolerances, as can the corresponding number of streams and lakes to be sacrificed.

To illustrate the implications of this process, and the role of predictive response models in providing options, Table 3-12 summarizes the evidence available and the projected consequences of SO_4^{2-} loadings at three different intensities, using three different models of the response. The loading levels are:

1. 5 kg/ha/yr - a level only slightly above the apparent historic levels of SO_4^{2-} deposition in northern, interior, continental land masses;

2. 15 kg/ha/yr - a level reflecting somewhat elevated SO_4^{2-} deposition, and covering very large areas of the eastern and interior U.S. and Canada; and

3. 45 kg/ha/yr - a level representative of the heavily acid SO_4^{2-} impacted regions of the eastern U.S. and Canada.

The results shown in Table 3-12 are literal interpolations of prospective responses, using the three models discussed previously. The limitations of incomplete data bases and validation steps must be heeded, but there is considerable consistency in the projections. Biological responses range from negligible to significant for the most sensitive streams or lakes, with SO_4^{2-} loadings ranging from 5 to 15 kg/ha/yr. Effects are less extreme in moderately to only slightly sensitive streams and lakes. Thus, the tools presently available appear to be adequate to begin a discussion of the resource impacts which may have to be accpeted in an analysis of trade-offs with abatement costs.

AQUATIC AREAS SENSITIVE TO ACIDIC DEPOSITION POSSIBLY RESULTING FROM TRANSBOUNDARY AIR POLLUTION

STREAMS/LAKES, UNITED STATES

Minnesota, Wisconsin, and Michigan

Northern areas of Minnesota, Wisconsin, and Michigan are potentially susceptible to acid deposition (Galloway and Cowling, 1978), because coarse-textured soils there are very low in calcium carbonate, and are underlain by acidic igneous and metamorphic bedrocks and poorly buffered sandstone. The region's rich resources and related industries, including recreation, forestry, farming, and mining would be vulnerable to disruption if acid inputs reached levels presently being experienced in other areas of the United States.

The overall high water quality of Minnesota, Michigan, and Wisconsin is basic to the economical and natural resources of the region. The headwaters of the Mississippi River, the Great Lakes Drainage Basin, and parts of the Hudson Bay drainage rise in this area. Protection of water quality for Lake Superior and for the Upper Mississippi River Basin has been a matter of vital concern to many Midwestern states for

TABLE 3-12

ILLUSTRATIVE DOSE/RESPONSE/TIME RELATIONSHIPS UNDER SELECTED LOADING PATTERNS

Projected Precipitation Quality	Projected Surface Water Quality	Projected Aquatic Effects
1. SO_4^{2-} Loading: Natural to 5 kg/ha/yr and 85 cm precipitation per year:		
Annual average pH 5.2 to 6.5	Dickson Relation: Minor pH, aluminum and heavy metal changes in very sensitive lakes.	Dickson: Probably no biotic effects.
Henriksen: Annual average pH 5.0	Henriksen Nomograph: No expected changes in lake status.	Henriksen: Probably no biotic effects.
	Episode Receptor/Dose: pH depression up to 0.7 units in very sensitive systems; up to 0.25 pH units change in moderately sensitive systems.	Receptor: Possible fish mortality in some years in very sensitive systems if pH depression coincides with sensitive life stages. No biotic effects moderately sensitive lakes.
2. SO_4^{2-} Loading: 15 kg/ha/yr and 85 cm precipitation per year:		
Annual average pH 4.6 to 4.8; single episodes to pH 4.2	Dickson: An average of 1 unit pH change for very senstive lakes; minor to no pH changes for moderately sensitive lakes.	Dickson: Fish mortality in very sensitive lakes; no known biotic effects moderately sensitive lakes.
Henriksen: Annual average pH 4.5	Henriksen: Ca. 30% of lakes in Norwegian study area would become acidified.	Henriksen: Potential fish mortalities in ca. 30% of lakes in study area due to acid conditions and elevated aluminum concentrations. Shifts in other native populations.
	Episode Receptor/Dose: Ca. 1.0 pH unit depression during episodes in very sensitive streams; near 0.5 pH unit depression in moderately sensitive lakes.	Fish mortality in very sensitive systems if pH depression coincides with sensitive life history stages.

TABLE 3-12 (Continued)

ILLUSTRATIVE DOSE/RESPONSE/TIME RELATIONSHIPS UNDER SELECTED LOADING PATTERNS

Projected Precipitation Quality	Projected Surface Water Quality	Projected Aquatic Effects
3. SO_4^{2-} Loading: 45 kg/ha/yr and 85 cm precipitation per year:		
Annual average pH	Dickson: An average of 1 to 2 unit pH changes for very sensitive lake; 1 unit change for moderately sensitive lakes.	Dickson: Metal mobilization and elimination of sensitive species from very sensitive lakes; major shifts in populations in very sensitive lakes; partial mortality of sensitive biota in moderately sensitive lakes.
Henriksen: Annual average pH 4.08	Henriksen: Approximately 90% of lakes in Norwegian study area appear to become acidified.	Henriksen: Potential fish mortalities in 90% of lakes in study area due to acid conditions and elevated aluminum concentrations; shifts in natural populations; elimination of sensitive biota from most sensitive lakes.
	Episode Receptor/Dose: ca. 1.5 pH unit depression in very sensitive systems; ca. vicinity of 0.6 pH unit depression in slightly sensitive systems.	Elimination of sensitive biota from very sensitive systems; major shifts in natural populations; partial mortalities in moderately sensitive systems due to heavy metal and aluminum mobilization.

many decades. The western portion of the three-state region and adjacent Ontario gives rise to the Rainy River Basin, which eventually flows to Manitoba, and thence to Hudson Bay.

Available estimates indicate that Minnesota has from 15,000 to 22,000 lakes, covering 4,000 square miles. Half the lakes in the BWCAW are susceptible to acidification, due to low buffering capacity associated with alkalinities below 200 microequivalents per litre. Wisconsin has some 11,000 lakes more than 20 acres in size, and 2,600 lakes have a pH at or below 6.0 with little or no alkalinity, (Glass, 1980). Michigan has more than 10,000 lakes over 10 acres in size, and susceptible to acidification. Of some 8,000 lakes and ponds in the western half of the upper peninsula of Michigan, more than 50 percent have an alkalinity in the range of 10 ppm, indicating that they are potentially susceptible to acid inputs.

Wisconsin has 2,250 trout streams, totalling 8,690 miles; data for the other two states were not available at the time of writing, but are likely to be similar.

The state of Wisconsin estimates use of state-owned parks and forests at more than 11 million visitors per year, for 1971 to 1973 (the most recent statistic available). The 1979 estimated value of 4.8 billion dollars, for the tourist industry, is related to the aquatic resources, and second only to agriculture in dollar size. More than 10 million tourists visit the state of Michigan each year. Data for these state and federally owned services, however, represent only a small part of the total investment in services to the public by the recreation industry in these states. The loss of even a small number of lakes or streams in this region would adversely affect individual services directly, thereby influencing the industry to some degree; how much, is a matter of considerable concern to each of the states involved.

New England

A preliminary analysis of 300 headwater ponds and streams in the six New England states shows that alkalinity readings of less than 200 microequivalents per litre (μeq/l) cover most of the regions examined, with widespread readings below 20 μeq/l (Figure 33). For comparison, Thompson and Elder (1981) have considered lakes with alkalinity readings below 200 μeq/l as highly sensitive to acidification (Haines, in press).

Adirondack Region of New York

A survey of 214 higher elevation lakes of the Adirondack Mountains area of New York shows that all surveyed lakes are very sensitive to acidification (less than 200 μeq/l alkalinity), and that many are already acidified, as indicated by the negative alkalinities (Figure 34).

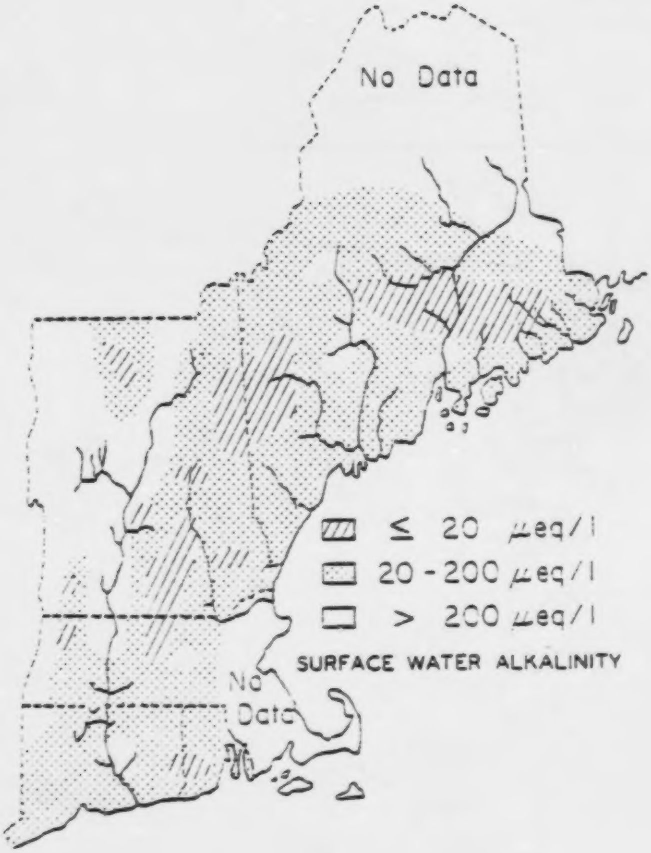
No Data
▨ ≤ 20 µeq/l
▩ 20 - 200 µeq/l
☐ > 200 µeq/l
SURFACE WATER ALKALINITY
No Data

Figure 33. Surface water alkalinity of New England states (Haines, in press).

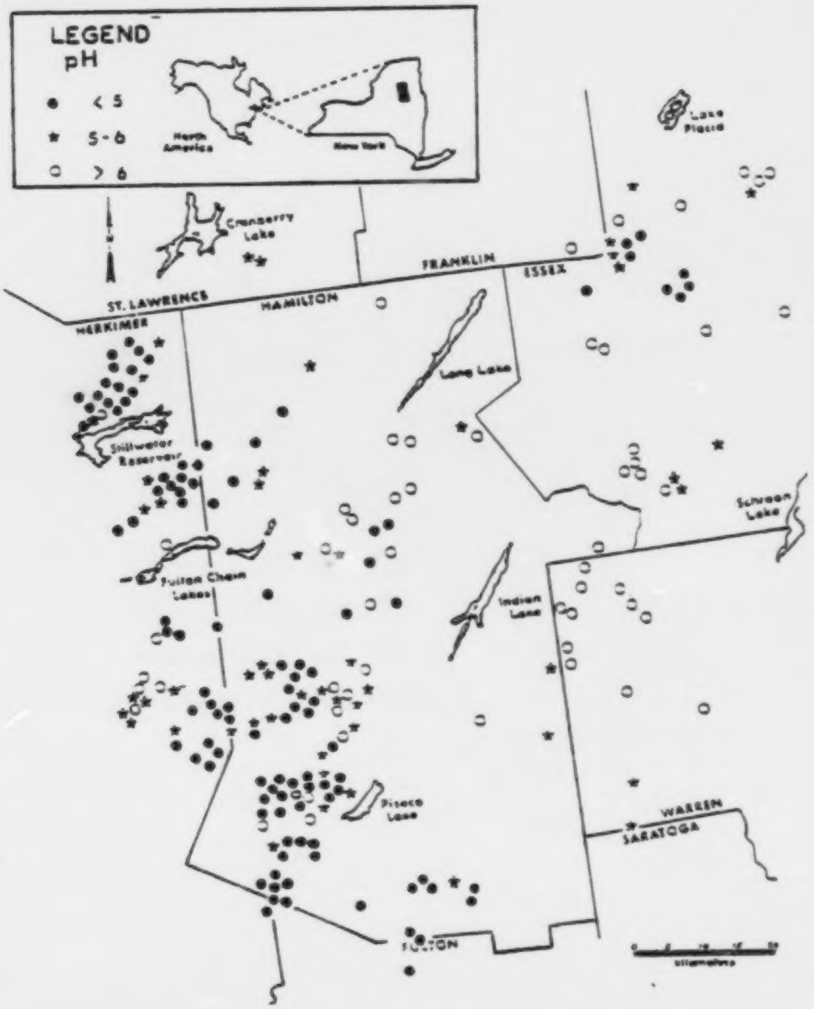
LEGEND
pH
● < 5
★ 5-6
○ > 6
North America
New York
Cranberry Lake
Lake Placid
FRANKLIN
ESSEX
ST. LAWRENCE
HAMILTON
HERKIMER
Long Lake
Stillwater Reservoir
Fulton Chain Lakes
Indian Lake
Schroon Lake
Piseco Lake
WARREN
SARATOGA
FULTON
kilometers

Figure 34. Geographic distribution of pH levels measured in Adirondack lakes higher than 610 meters elevation, June 24-27, 1975 (Schofield, 1976).

New Jersey

Over the last 17 years, a decline of pH, amounting to 0.4 unit has been observed in headwater streams draining the Pine Barrens (Johnson, 1979). Soils in this area are largely sandy, with little buffering or neutralization capacity. This is probably the explanation for the very acid groundwater. An average pH of 4.3 was found for the years 1978 and 1979.

North Carolina

A study of changes in stream chemistry, between the early 1960's and 1979 (a 15 to 19 year period), in western North Carolina, shows that pH dropped from 6.77 to 6.51, representing an 87% increase in hydrogen ion concentration. Over the same period, mean alkalinity declined 31%. In the analysis, the differences in the methods used in the 1960's and in 1979 were accounted for, in order to eliminate sampling biases.

In the Great Smoky Mountains National Park, other symptoms have been observed in an independent study. Acid runoff at pH's as low as 4.1, in perennial mountain streams, has produced elevated aluminum concentrations. Inhibiting effects upon population densities of benthic macroinvertebrates, and upon brook trout populations, have been connected to sulphuric acid loadings. Similarity of edaphic conditions in the park, and in the Adirondack Lake region of New York, was noted.

STREAMS/LAKES, CANADA

Ontario

About 6% of 1,527 lakes recently surveyed in Ontario were classified as acidified. These lakes were found to have an alkalinity rating equal to, or less, than 0 microequivalents per litre (μeq/l). An additional 12% (187 lakes) were classified as extremely sensitive, and a further 43% (482 lakes) were considered moderately sensitive (Table 3-13). Based on lake alkalinity data, it is reasonable to expect that up to 30% of the lakes in the important tourist areas of Muskoka-Haliburton will be acidified, by present acid loadings, although the time scale cannot yet be defined. Data for the Manitoulin and Sudbury Districts must be interpreted with some caution since those areas were subjected to local problems related to smelting operations in Sudbury. Scheider et al., (1980), and Chan et al., (1980), indicate that long-range transport of acid to the area is substantial, but its influence relative to the historic local problems, with respect to acidifying lakes, cannot be determined.

Quebec

Vast areas of Quebec, north of the St. Lawrence Valley, have largely sensitive, low buffered waters (Figure 35). Detailed surveys are not

Table 3-13 Summary of the Percentage of Lakes in each Alkalinity Class by County or District and for Ontario.

County or District	Percentage of Total No. of Lakes in each Alkalinity Class					Total No. of Lakes
	Acidified (≤ 0 *ueq/l*)	Extreme Sensitivity (> 0 to 39.9 *ueq/l*)	Moderate Sensitivity (40 to 199 *ueq/l*)	Low Sensitivity (200 to 499 *ueq/l*)	Not Sensitive (≥ 500 *ueq/l*)	
Algoma Dist.	5	11	30	28	26	163
Bruce Co.					100	7
Cochrane Dist.		7		11	82	27
Durham Co.					100	1
Frontenac Co.				6	94	64
Grey Co.					100	3
Haliburton Co.		24	39	22	15	112
Hastings Co.			21	11	68	63
Huron Co.					100	1
Kenora Dist.			14	25	61	88
Lanark Co.					100	15
Leeds Co.					100	24
Lennox & Addington Co.			36	12	52	25
Manitoulin Dist.	52	29	3	3	13	31
Middlesex Co.					100	1
Muskoka Dist.	1	30	61	2	6	115
Nipissing Dist.		9	75	13	3	75
Northumberland Co.					100	1
Ontario Co.					100	5
Parry Sound Dist.	5	20	64	10	1	107
Peel Co.					100	1
Peterborough Co.		4	16	6	74	49
Prince Edward Co.					100	3
Rainy River Dist.		3	64	19	14	99
Renfrew Co.			8	32	60	50
Simcoe Co.					100	7
Stormont Co.					100	1
Sudbury Dist.	24	29	23	12	12	210
Thunder Bay Dist.	1	2	25	27	45	136
Timiskaming Dist.	13		7	27	53	30
Victoria Co.					100	11
York Co.					100	2
Province	6	12	31	16	35	
(No. of Lakes)	(87)	(187)	(482)	(241)	(530)	1,527

From Ontario Ministry of Environment

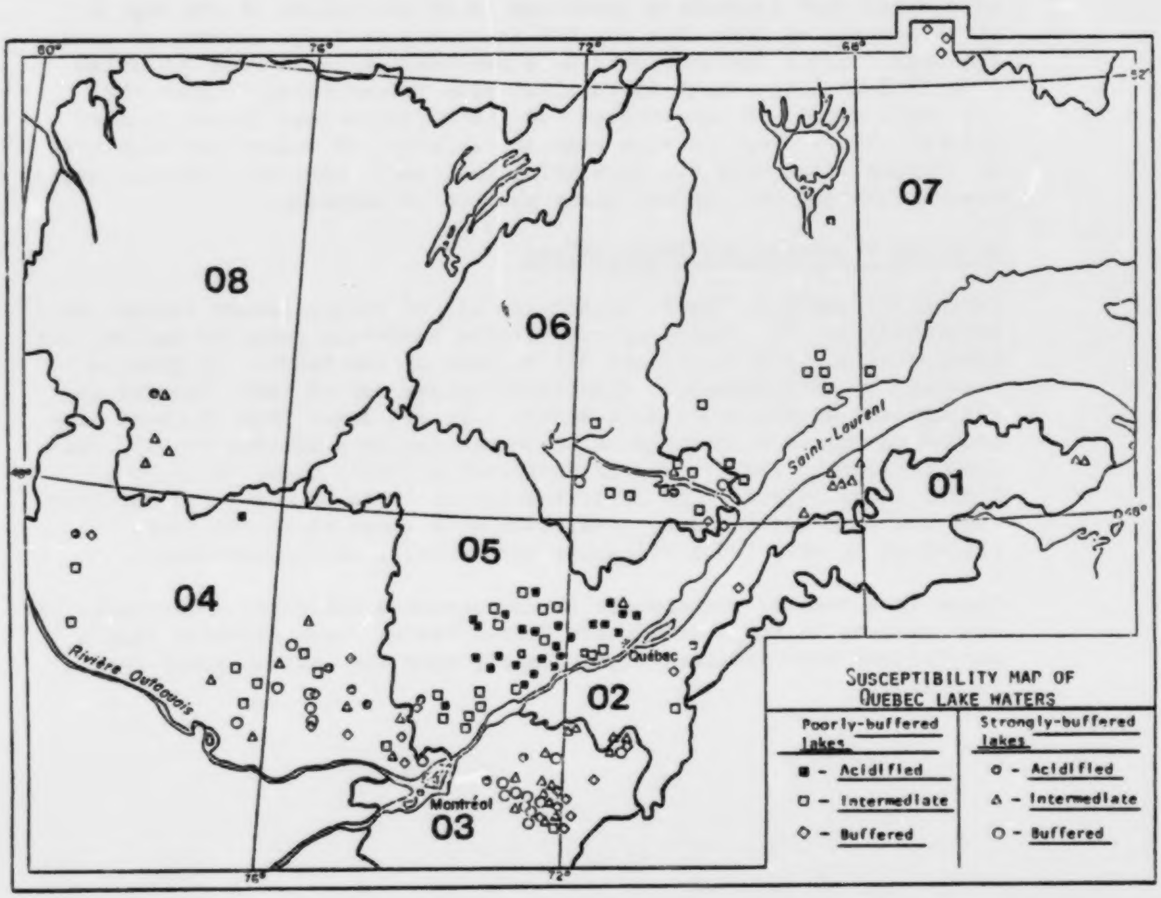
60°
76°
72°
68°
52°
48°
08
07
06
05
04
03
02
01
Saint-Laurent
Rivière Outaouais
Québec
Montréal
76°
72°
SUSCEPTIBILITY MAP OF QUEBEC LAKE WATERS
Poorly-buffered lakes
■ - Acidified
□ - Intermediate
◇ - Buffered
Strongly-buffered lakes
○ - Acidified
△ - Intermediate
○ - Buffered

Figure 35. Susceptibility map of Quebec lake waters (Environment Canada, 1980).

yet available for most of the large numbers of lakes of this province. Surveys of lake waters in southern Quebec (Environment Canada, 1980), classified according to the model of Henriksen (1979), show that nearly all lakes classified as weakly buffered are also considered acidified by the Henriksen criteria. Furthermore excess sulphate originating from acid rain deposition, has been found in precambrian lakes north of the St. Lawrence river and especially north of Hull and north west of Quebec city. In this latter area up to 41 per cent of the 58 lakes studied showed very high excess sulphates and most of these lakes had pH value less than 5.7 (Legendre et al., 1980).

Labrador

Labrador, as part of the Canadian Shield, is composed mostly of granite with basic rock intrusions found mostly in the centre of the region. It is covered by very thin topsoil and contains large numbers of sphagnum bogs. Major ion chemistry data has been gathered from 400 sites from 1978 to 1980, which shows alkalinity values rarely higher than 150 μeq/l except on anorthosite and gabbro intrusions (Water Quality Branch, 1981). Despite such high sensitivity, pH values are high with an average value near 6.4 suggesting that until now, acid precipitation has not changed the surface water quality of Labrador.

Maritime Provinces and Newfoundland

Except for northern New Brunswick and all of Prince Edward Island, most watersheds in this region provide little buffering capacity against acid precipitation (Figures 36 and 37) as much of the bedrock is granite overlain by thin podzols. Alkalinity values for 63 lakes located in eastern and southwestern Nova Scotia were all lower than 50 μeq/l with summer pH values of certain weirs decreasing to a minimum of 4.5 (Water Quality Branch, 1981). Use of Henriksen's (1979) model on 16 Nova Scotia lakes suggest that acidification of 40 to 50 μeq/l has occurred over the past two decades, consistent with measured pH declines, (Thompson et al., 1980; Wiltshire and Machell, in preparation).

These lake results corresponde to concurrent acidification decreases of weir systems in the southwestern United States where Atlantic salmon populations have declined significantly over the last 30 years (Watt, in press).

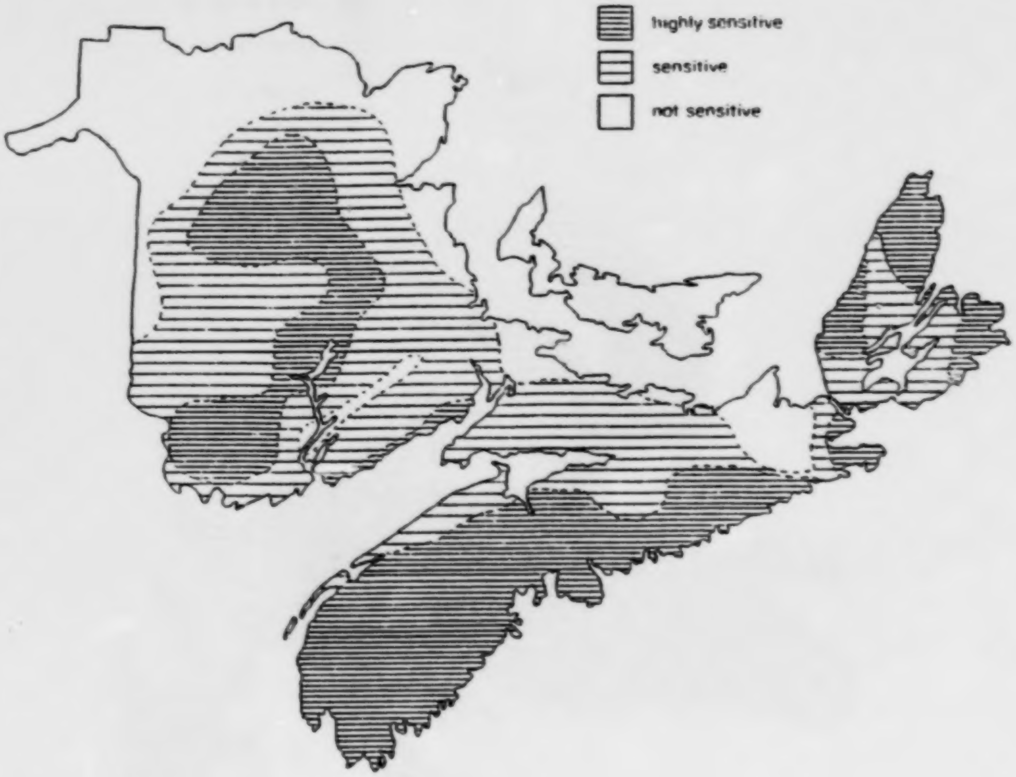
highly sensitive
sensitive
not sensitive

Figure 36. Sensitivity to acidification of surface waters in the Maritime Provinces (modified from Clair, 1979).

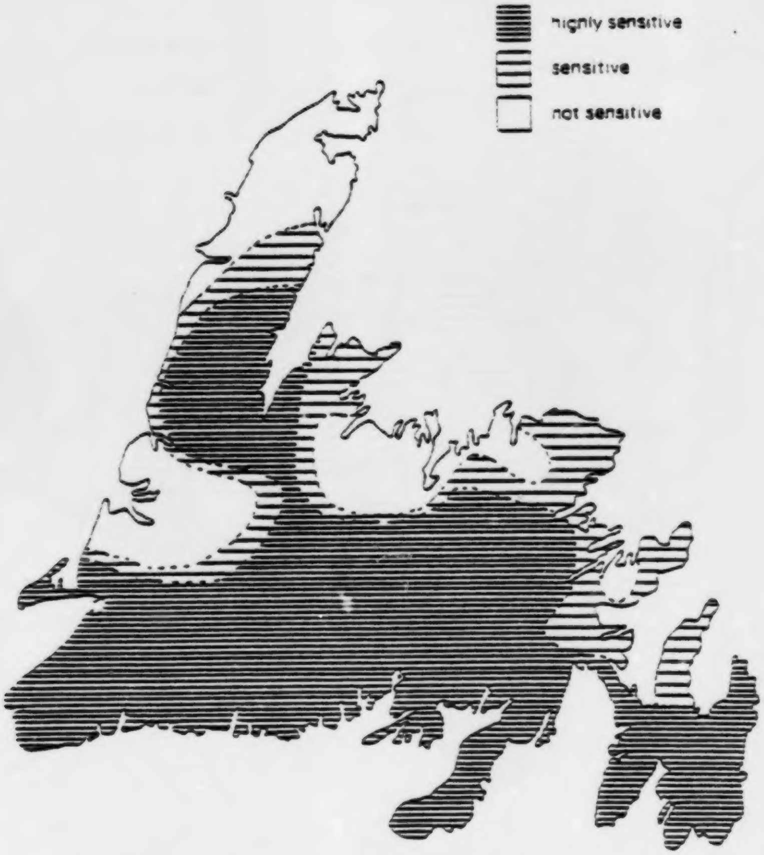
highly sensitive
sensitive
not sensitive

Figure 37. Sensitivity to acidification of surface waters in insular Newfoundland (modified from Clair, 1979).

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SECTION 4

TERRESTRIAL IMPACTS

INTRODUCTION

A number of air pollutants, generated by various sources, cross international, state and provincial boundaries. The main pollutants which are, or have the potential to be, harmful are oxides of sulphur, oxides of nitrogen, particulates, and secondary products, such as oxidants and acid precipitation.

Sulphur dioxide (SO_2) is emitted at relatively high concentrations by a large number of sources, including power plants and smelters. Most of this SO_2 may be deposited near the sources, or may be transformed chemically in the atmosphere to other sulphur compounds, particularly SO_4^{2-}. A moderate amount of SO_2 remains in the atmosphere, to be widely distributed as such. However, in areas remote from the source, the concentration of SO_2 near the ground is close to background levels, and not likely to cause adverse direct effects. By oxidation to SO_4^{2-}, and hydrolysis to sulphuric acid, however, SO_2 contributes to the formation of the secondary pollutant, acid precipitation. Similarly, ozone (O_3) is also a secondary pollutant, since it is not emitted directly, but is formed in the atmosphere in the presence of sunlight, after chemical transformations of nitrogen dioxide and reactive hydrocarbons.

In summary, both acid precipitation and O_3 are long-range, transported pollutants, since they occur in high concentrations in ambient air, at distances of hundreds of kilometers from the sources of the precursor pollutants.

Direct effects on vegetation are well known and documented for SO_2 and O_3, as a result of observations made in the field and in laboratory experiments (Linzon, 1981). It is stressed that, at present, only experimental evidence is available for direct effects of acid precipitation on vegetation, with no direct effects having been documented conclusively in the field for vegetation exposed to ambient precipitation. However, direct effects on soils have been observed. Further, acid precipitation contains plant nutrients; thus, beneficial as well as harmful effects must be considered.

This section on terrestrial effects of transboundary air pollutants is presented in four parts: (1) direct effects on vegetation; (2) indirect effects on vegetation; (3) effects on soils; and (4) sensitivity assessment.

DIRECT EFFECTS ON VEGETATION

Direct effects of atmospheric pollutants on terrestrial plants may be addressed through consideration of the impacts of O_3 and acid precipitation, the latter being derived from both sulphur and nitrogen compounds.

Terrestrial plants have the capacity to take chemical elements directly from the atmosphere. In cases where these are nutrients deficient in the growth medium, growth stimulation may occur. In some cases, elements removed from the atmosphere may be harmful. Thus, this same facility for removing elements from the atmosphere may also be harmful.

Ozone

Ozone is now recognized as the major component of photochemical smog and a major direct phytotoxicant in the smog complex (Richards et al., 1958). Visible foliar injury, resulting from exposure to atmospheric ozone, is apparent either as pigmented lesions, bleaching, topical necrosis and/or general chlorosis (Hill et al., 1970). Plant leaves ranging from 65-95% of full size are the most sensitive. Other factors affecting injury include numerous environmental factors, (eg. temperature, humidity and light) and the concentration, duration and exposure frequency.

Ozone injury to vegetation has been well documented on many crop species in North America, such as tobacco, beans, potatoes, grapes, onion, cucumber, celery, pumpkin, squash and radish. At ambient concentrations of ozone of .05 to .10 ppm during continuous or intermittent exposure periods, loss of plant fresh and dry weight may approach 15-30%, and yield losses of 5-10% may occur (Reinert, 1975). Experimental results for specific crops are listed in Table 4-1.

Acid Precipitation

Oxidation of SO_2, and hydrolysis to sulphuric acid, contribute to the formation of acid precipitation, which can affect terrestrial vegetation directly or indirectly. Hydrolysis of oxides of nitrogen to form nitric acid further contributes to the acidity of precipitation. Direct effects are the consequences of the interaction of the acid precipitation with the surfaces of the above-ground portions of the plant. The most common parameter measured is the degree and type of injury to the leaf, together with the measurement of physiological or morphological response.

Tamm and Cowling, (1977) prepared a partial list of theoretical direct effects of acid precipitation on vegetation, in which a decreased rate of growth is the expected consequence. These effects are outlined below:

1. Damage to protective surface structures, such as cuticle;
2. Interference with normal functions of guard cells;

TABLE 4 -1. EFFECTS OF LONG-TERM CONTROLLED OZONE EXPOSURES ON GROWTH, YIELD, AND FOLIAR INJURY TO SELECTED PLANTS

Plant Species	Ozone Concentration $\mu g/m^3$ (ppm)	Exposure time, hr	Plant response, percent reduction from control	Reference
Lemna, duckweed	196 (0.10)	3/day, 14 days	100, flowering; 36, flowering (1 wk after exposure completed) 30, frond doubling rate	(Feder & Sullivan,1969)
Carnation	98-177 (0.05-0.09)	24/day, 90 days	50, flowering (reduced vegetative growth)	(Feder, 1970)
Geranium	137-196 (0.07-0.10)	9.5/day, 90 days	50, flowering (shorter flower lasting time, reduced vegetative growth)	
Petunia	98-137 (0.05-0.07)	24/day, 53 days	30, flower fresh wt	(Craker, 1972)
Poinsettia	196-235 (0.10-0.12)	6/day, 5 days/week, 10 weeks	39, bract size	(Craker & Feder, 1972)
Radish	98 (0.05)	8/day, 5 days/week, 5 weeks	54, root fresh wt 20, leaf fresh wt	(Tingey et al, 1971)
	98 (0.05)	8/day, 5 days/week (mixture of O_3 and SO_2 for same periods)	63, root fresh wt 22, leaf fresh wt	
Beet, garden	392 (0.20)	3/day, 38 days	50, top dry wt	(Ogata & Maas, 1973)
Bean, cultivar Pinto	255 (0.13)	8/day, 28 days	79, top fresh wt 73, root fresh wt 70, height	(Manning et al, 1971)
Bean, cultivar Pinto	290 (0.15)	2/day, 63 days	33, plant dry wt; 46, pod fresh wt	(Hoffman et al, 1973)
	490 (0.25)	2/day, 63 days	95, plant dry wt; 99, pod fresh wt	
	686 (0.35)	2/day, 63 days	97, plant dry wt; 100, pod fresh wt	
Bean, cultivar Pinto	290 (0.15)	2/day, 14 days	8, leaf dry wt	(Maas et al, 1973)
	290 (0.15)	3/day, 14 days	8, leaf dry wt	
	290 (0.15)	4/day, 14 days	23, leaf dry wt (Data available on whole plants, roots, leaves, injury, and	
	290 (0.15)	6/day, 14 days	49, leaf dry wt 3 levels of soil moisture stress)	
	440 (0.225	2/day, 14 days	44, leaf dry wt	
Bean, cultivar Pinto	440 (0.225)	4/day, 14 days	68, leaf dry wt (Data available on whole plants, roots,	(Maas et al, 1973)
	588 (0.30)	1/day, 14 days	40, leaf dry wt leaves, injury and 3 levels of soil	
	588 (0.30)	3/day, 14 days	76, leaf dry wt moisture stress)	
Tomato	392 (0.20)	2.5/day, 3 days/week 14 weeks	1, yield; 32, top dry wt; 11, root dry wt	(Oshima et al, 1975)
	686 (0.35)	2.5/day, 3 days/week, 14 weeks	45, yield; 72, top dry wt; 59 root dry wt	
Corn, sweet cultiver Golden Jubilee	392 (0.20)	3/day, 3 days/week till harvest	13, kernel dry wt; 20, top dry wt; 24, root dry wt	(Oshima, 1973)
	686 (0.35)	3/day, 3 days/week till harvest	20, kernel dry wt; 48, top dry wt; 54, root dry wt	
Wheat, cultivar Arthur 71	392 (0.20)	4/day, 7 days (anthesis)	30, yield	(Kochar, 1974)
Soybean	98 (0.05)	8/day, 5 days/week 3 weeks	13, foliar injury	(Tengey et al, 1973)
		8/day, 5 days/week (mixture of O_3 and SO_2 for same periods)	16, foliar injury 20, root dry wt	
Soybean	196 (0.10)	8/day, 5 days/week 3 weeks	21, top dry wt 9, root dry wt	
Alfalfa	196 (0.10)	2/day, 21 days	16, top dry wt	(Hoffman et al,1974)
	290 (0.15)	2/day, 21 days	26, top dry wt	
	390 (0.20)	2/day, 21 days	39, top dry wt	
Grass, brome	290-647 (0.15-0.33)(varied)	4/day, 5 days/week growing season	83, biomass	(Price & Treshow, 1972)
Alfalfa	196 (0.10)	6/day, 70 days	4, top dry wt, harvest 1 20, top dry wt, harvest 2 50, top dry wt, harvest 3	(Neeley et al, 1977)
Alfalfa	98 (0.05)	7/day, 68 days	30, top dry wt, harvest 1 50, top dry wt, harvest 2	
Alfalfa	98 (0.05)	8/day, 5 days/week 12 weeks	18, top dry wt	(Tingey & Reinert, 1975)
Pine, eastern white	196 (0.10)	4/day, 5 days/week 4 weeks (mixture of O_3 & SO_2 for same periods)	3, needle mottle (over 2-3 days of exposure)	(Dochinger & Seliskar, 1970)
Pine, ponderosa	290 (0.15)	9/day, 10 days	4, photosynthesis	(Miller et al, 1969)
	290 (0.15)	9/day, 20 days	25, photosynthesis	
Pine, ponderosa	290 (0.15)	9/day, 30 days	25, photosynthesis	
	290 (0.15)	9/day, 60 days	34, photosynthesis	
	588 (0.30)	9/day, 10 days	12, photosynthesis	
	588 (0.30)	9/day, 20 days	50, photosynthesis	
	588 (0.30)	9/day, 30 days	72, photosynthesis	
	880 (0.45)	9/day, 30 days	85, photosynthesis	

Table 4-1 (cont'd). EFFECTS OF LONG-TERM CONTROLLED OZONE EXPOSURES ON GROWTH, YIELD, AND FOLIAR INJURY TO SELECTED PLANTS

Poplar, yellow	588 (0.30)	8/day, 5 days/week 13 weeks	82, leaf drop; 0, height	(Jensen, 1973)
Maple, silver	588 (0.30)	8/day, 5 days/week, 13 weeks	50, leaf drop; 78, height	
Ash, white	588 (0.30)	8/day, 5 days/week 13 weeks	66, leaf drop; 0, height	
Sycamore	588 (0.30)	8/day, 5 days/week 13 weeks	0, leaf drop; 22, height	
Maple, sugar	588 (0.30)	8/day, 5 days/week 13 weeks	28, leaf drop; 64, height	
Corn, sweet, cultivar Golden Midget	98 (0.05)	6/day, 64 days	9, kernal dry wt; 14, injury (12, avg. 4 yield responses)	(Heagle et al, 1972)
	196 (0.10)	6/day, 64 days	45, 25, 35 for same responses	
Pine, ponderosa	196 (0.10)	6/day, 126 days	12, root length 21, stem dry wt; 26, root dry wt	(Wilbour & Neely, 1977)
Pine, western white	196 (0.10)	6/day, 126 days	13, foliage dry wt 9, stem dry wt	
Soybean, cultivar Dare	98 (0.05)	6/day, 133 days	3, seed yield; 22, plant fresh wt 19, injury, defoliation, no reduction in growth or yield	(Heagle et al, 1974)
	196 (0.10)	6/day, 133 days	55, 65, 36 for same responses	
Poplar, hybrid	290 (0.15)	8/day, 5 days/week 6 weeks	50, shoot dry wt; 56, leaf dry wt 47, root dry wt	(Jensen & Dochinger, (1974)

(U.S. EPA, 1978)

3. Poisoning of plant cells after diffusion of acidic substances through stomata or cuticle;
4. Disturbance of normal metabolism or growth processes, without necrosis of plant cells;
5. Alteration of leaf- and root-exudation processes;
6. Interference with reproduction processes;
7. Synergistic interaction with other environmental stress factors.

Evidence of significant growth effects from ambient acid loadings, under field conditions, has yet to be demonstrated; however, effects of simulated acid rain are evidenced by foliar injury, canopy reduction and decreased yield, although some species show increased yield in mid-pH ranges. The possibility of growth benefit, particularly in upland forest ecosystems, and particularly in response to N-addition, cannot be discounted in light of small, but continuing, additions of NO_3^- in acid precipitation. Loading rates in high impingement areas might approach 5-10 kgN/ha/yr. Total N-flux in mid-age jack pine forest in Northern Ontario, for example, a system typically responding to N-fertilizers, is in the order of 40 kgN/ha/yr (Foster and Morrison, 1981).

Generally, however, each species has a unique pattern of sensitivity to acid precipitation, although it is often difficult to establish or replicate the thresholds. This is due to variability in the growth conditions between and within studies. Table 4-2 lists representative plant tolerances to acid precipitation.

Throughfall: Filtering and Leaching Effects

Reviews of filtering and leaching effects are presented in recent working papers (Singh et al., 1981; Cowell et al., 1981; Morrison et al., 1981).

A wide variety of organic and inorganic substances can be leached from foliage, and the process can be important to the proper growth and development of plants.

Precipitation undergoes chemical alteration on contact with leaves, both on the surface, and, indirectly, within cellular tissue. As well, dry deposition on plant surfaces is involved. The nature of the leachate or throughfall depends upon plant characteristics, such as tree species and leaf morphology, and stand characteristics, such as age and stocking on the one hand, and site conditions, including precipitation rate, distribution and chemical composition, on the other. Input/output analyses and element budgets have been described by various authors

TABLE 4-2. REPRESENTATIVE TOLERANCE LIMITS TO SIMULATED ACID PRECIPITATION

Species	Pollutant Concentration	Effect	Source
birch	pH 2.0-2.5	- foliar lesions	Abrahamsen et al., 1976
willow herb			
Scots pine			
mosses	pH 3.0		
lichens	pH 4.0	- reduced N fixation rate	Dennison et al., 1976
sunflower, bean	pH 2.7	- foliar damage	Evans et al., 1977
hardwoods	pH 2.5	- foliar damage	Haines and Waide, 1980
wheat, grasses	pH 4.0	- root biomass reduction	Lee and Weber, 1980
radish	pH 3.5	- foliar damage	Lee et al., 1980
beet	pH 4.0		
carrot	pH 4.0	- reduced yield	
mustard greens	pH 3.5	- foliar damage and reduced marketability	
spinach			
swiss chard			
tobacco	pH 3.5	- foliar damage	
lettuce			
broccoli/cauliflower	pH 3.5	- foliar damage	
cabbage	pH 3.0		
broccoli	pH 3.0	- reduced yield	
potatoes	pH 3.0	- foliar damage reduced yield	
	pH 3.5-4.0	- increased yield	
alfalfa	pH 3.5	- foliar damage	
	pH 3.5-4.0	- increased yield	
kidney beans, oak	pH 3.2	- inhibition of parasitic organisms	Shriner, 1976
conifer seedlings	<pH2.0	- foliar damage	Strifler & Kuehn, 1976
mosses	pH 2.0 - 3.0	- dessication, death	Teigen et al., 1976
chrysanthemums	pH 3.0	- foliar damage and increased phosphate uptake	Tukey, 1980
juniper	pH 4.0+		
yellow birch	pH 2.3-4.7	- pitting, curl shortening, death	Wood and Bormann, 1974

1/ The average precipitation pH in eastern North America is currently greater than or equal to pH 4.0. Individual storm events may have episodes where the pH drops into the range of pH 3.0 to 4.0.

(Lakhani and Miller, 1980; Mayer and Ulrich, 1980; Tukey, 1980, and others). Generalizations are difficult, because of the wide range of environmental (soil, water, climate) conditions.

Spruce canopies have been found to filter dry pollutants from the atmosphere better than deciduous canopies. This is attributed, in part to, the presence of spruce needles throughout the winter, during which SO_2 is dissolved in water films adhering to their surfaces. Subsequent removal of these deposits accounts, in part, for difference in chemical composition of the throughfall.

Not all elements are leached equally, and, although all plant parts can be leached, young leaves are less susceptible than mature foliage (Tukey, 1980). Leaves only need to be wetted to initiate leaching, with further increases in precipitation having little additional effect. As cation removal increases over time, it is suggested that, only with adequate nutrient supply are plants able to withstand brief, frequent rain effects. Based on preliminary studies under spruce, it appears that leaching of Ca^{2+} and Mg^{2+} is pH dependent in the range pH 7.0 to 3.0.

Some researchers have found that throughfall from deciduous forest exhibits increased pH and higher Ca^{2+} and Mg^{2+} concentrations when compared to the incident precipitation. In other studies, the opposite has been found. In studies of two hardwood forests (sugar maple and red alder), little difference in throughfall chemistry was reported (Lee and Weber, 1980). Stemflow from birch species shows increased acidity, relative to the incident precipitation (Abrahamsen, Horntvedt and Tveite, 1977). Beneath coniferous canopy, throughfall pH generally decreases, relative to precipitation in open areas, although concentrations of Ca^{2+} and Mg^{2+}, as well as many other dissolved ions, may increase (Horntvedt and Joranger, 1976). This ion enrichment is due to both washout of dry deposits, and canopy leaching. It has been reported that 90% and 70% of the H^+ in precipitation was retained in the forest canopy in New Hampshire northern hardwood (Hornbeck et al., 1977) and Washington Douglas fir forests, respectively (Cole and Johnson, 1977). Leaching of low molecular weight organic acids from the canopy, on the other hand, acts to decrease the pH of throughfall (Hoffman et al., 1980).

Contact of precipitation with vegetation results in repartitioning of chemical components, in that substances in precipitation can be absorbed by the foliage, and substances in and on the foliage can be leached and recycled to the same plant or nearby plants. The direction of this exchange depends on the availability for exchange of a given component within each system, and permeability of plant surfaces to either uptake or egress. Throughfall studies demonstrate an enrichment of inorganic ions in the precipitation after contact with vegetation, with increasing losses of cations as the H^+ ion concentration in simulated precipitation increases. Laboratory experiments have demonstrated leaching in a wide variety of organic substances, including growth regulators, amino acids, carbohydrates and organic acids.

If such a leaching process is a simple exchange of H^+ ions for cations, then the fate and effect of increasing H^+ ion concentration in plant tissue is a question that deserves some consideration. Further, if increasing rainfall acidity is providing excess H^+ ions for foliar cation exchange, exchangeable foliage cations may be depleted. However, if a portion of the leached elements remains in an available form, then root uptake may, in part, ameliorate these losses. Thus, soil conditions have considerable influence. Soil would also be a factor in determining the availability of leachable ions in foliage, and thus the degree of neutralization of throughfall acidity.

INDIRECT EFFECTS ON VEGETATION

Acid precipitation may also have many indirect consequences on vegetation. Tamm and Cowling, (1977) report that resistance and/or susceptibility to host pathogens, parasites, and insects may be altered by subjecting plants to any environmental stress. Acid precipitation may thus increase the susceptibility of plants to these injurious agents, alter their capacity to tolerate disease or injury, or alter their resistence to pathogens.

The effects of acid precipitation may vary with the nature of the pathogen involved (fungus, bacterium, mycoplasma, virus, nematode, parasitic, seed plant, insect, or multiple-pathogen complex), and with the stage in the disease cycle during which stress is applied. For example, acid rain might increase or decrease the infective capacity of bacteria before infection, or increase or decrease the susceptibility of the host to disease development afterwards (Shriner, 1980).

With regard to terrestrial wildlife, no conclusive evidence of deleterious effect has, as yet, been documented. However, with reference to the foregoing comments on chemical composition of vegetation in general, some concern, relative to its nutritional value, as browse, to various herbivores, has been expressed. White muscle disease, a physiological selenium disorder, resulting from increased sulphur intake, has been suggested as possible for large mammals browsing on vegetation enriched with sulphur.

EFFECTS ON SOIL

For this summary, the effects, or potential effects, of changes in precipitation composition and, in particular, of increased precipitation acidity, are discussed under the following headings:

(1) Decrease of Soil pH

(2) Increase of Base Leaching and Decrease in Base Saturation

(3) Mobilization of Trace Metals

(4) Clay Transformations

(5) Influence on Soil Biota and on Soil Biochemistry

(6) Influence on Organic Cycle

In addition, it must be recalled that soils vary widely with respect to their properties (physical, biological, chemical and mineralogical, etc.), support quite different vegetation communities, are subjected to different cultural practices, are situated in different climatic zones, and are exposed to a broad spectrum of acid loadings. Thus, caution must be exercised in generalizing from findings indicated herein. Further, there are various offsetting mechanisms, which may influence effects of increased precipitation acidity, and which, likewise, vary with soil properties, vegetation types, climatic regimes, cultural practices, etc. (Morrison et al., 1981).

Decrease of Soil pH

Soil acidification chiefly involves replacement of 'basic' (K^+, Ca^{2+}, Mg^{2+}, Na^+, etc.) cations by H^+ and, at lower pH levels, Al^{3+} ions. The chemistry of soil acidification is relatively well understood (Wiklander, 1973/74, 1975, 1980; Bache, 1980; Nilsson, 1980). The normal range of soil pH values and perceived acidities is given in Table 4-3. The normal range of pH for soils in humid regions is about pH 5.0 to 7.0, with the preferred range for cultivated soils generally about pH 6.0 to 7.0. Many natural soils, particularly under coniferous cover, fall within the range pH 4.5-5.5 in the mineral horizons, with surface organic layers commonly in the range 3.5-4.5.

An increase in soil acidity is considered detrimental to the chemical availability of several essential macro-nutrient elements (N, P, K, Ca, Mg). In addition, an increase of soil acidity can also lead to mobilization of certain other elements (for example Al, Mn, Fe), sometimes in toxic quantities. Some indication of the range of reactions involved, with reference to several of the common nutrient and non-nutrient elements, is given in Table 4-4.

With specific reference to acid precipitation, various experiments have been carried out, under both laboratory and field conditions in which it has been shown that, among other things, artificial acid rains of various pHs measurably decrease soil pH. For example, in a spruce podzol soil in Norway, simulated acid rain significantly depressed pH of the O, A and B horizons, in some cases by more than 0.5 pH units, as a function of cumulative acid input (Abrahamsen et al., 1976).

Natural soil acidification is an ongoing process in humid regions. Its impoverishing action is compensated for, in part, by weathering of the primary minerals and, where vegetated, by biological cycling of elements. Conifers have long been thought to increase soil acidity. Some

TABLE 4-3. TERMS USED (USDA) FOR DESCRIPTION OF SOIL ACIDITY

Term	pH Range
Neutral	6.6 - 7.3
Slightly Acid	6.1 - 6.5
Medium Acid	5.6 - 6.0
Strongly Acid	5.1 - 5.5
Very Strongly Acid	4.5 - 5.0
Extremely Acid	Below 4.5

TABLE 4-4. ACIDITY RELATED REACTIONS INFLUENCING AVAILABILITY OF SEVERAL ELEMENTS

Element(s)	Type of Reaction
N	Chiefly biological - biochemical; nitrifying bacteria decline with declining pH, thus ammoniacal-N predominates over nitrate-N
P	pH regulated ionization of the orthophosphates
K, Ca, Mg	Chiefly mass displacement of adsorbed bases by H+ ions
Fe, Mn	Chiefly dissolution of hydroxides in acid solution; organic status, redox important particularly for Fe
Al	pH regulated dehydroxylation of Al-hydroxides

indication of orders of magnitude of H^+ ion contribution by softwood, versus hardwood forest, and their relationship to anthropogenic loading, are available for at least one locality (Ulrich, 1980). Total H^+ ion input was determined as ca 0.81 keq/ha, of which 0.79 keq/ha was considered man-made. A beech canopy generated an additional ca 0.58 keq/ha; a spruce canopy, an additional 2.28 keq/ha. This evidence suggests that, as mean pH of rainfall declines below pH 4, its contribution to the H^+ ion balance is not insignificant, even in comparison to spruce forest production, thus hastening the process of acidification.

Increase of Base Leaching and Decrease in Base Saturation

Acidification and soil impoverishment involve the displacement of base cations (i.e. K^+, Ca^{2+}, Mg^{2+}, Na^+, etc.) from exchange surfaces, and their replacement by H^+ (and Al^{3+}) ions, and the establishment of new exchange/solution equilibria (Wiklander, 1973/74, and others).

Soils vary widely in ability to retain cations, (i.e. in cation exchange capacity (CEC)) and the relative degree of saturation of the CEC with bases, the latter being referred to as base saturation. Total CEC of a productive soil under cultivation, in humid regions, might range from 15-30 meq/100g, and occasionally higher, in the surface horizons, and decreasing to less than 1 meq/100g in the subsoil. In coniferous podzols, the CEC of the humus layer may be high, but, beneath it, values decrease abruptly with depth. It is presumed that the loss, particularly of those base cations of nutritive value (chiefly K^+, Ca^{2+}, Mg^{2+}), could be accelerated under acid precipitation, with attendant adverse impacts on forest growth.

Various 'simulated acid rain' leaching experiments are described in the literature (Abrahamsen et al., 1976; Abrahamsen and Stuanes, 1980; Roberts et al., 1980; Singh et al., 1980; Morrison, 1981; Lee and Weber, 1980).

Significant reductions of base saturation percentage were noted in the O and A horizons of spruce podzol soils, following applications of simulated acid rain with a pH of 4.0 or lower. Under natural conditions, two sets of processes seem to be involved. First, there are exchange processes whereby H^+ ions displace base cations from the exchange surface; and second, there are the processes whereby the exchanged ions are transported within the soil column, chiefly under the influence of anions (Johnson and Cole, 1976 and 1977).

In addition to the natural leaching anions, bicarbonate and organic anions, the principal leaching anion of anthropogenic origin would appear to be SO_4^{2-} from sulphuric acid. Some soils (chiefly those rich in Fe and Al sesquioxides) would appear to have substantial capacity to absorb SO_4^{2-} and, thus, exhibit considerable initial resistance to base leaching (Johnson and Cole, 1976; Johnson and Henderson, 1979; Roberts et al., 1980; Singh et al., 1980; Morrison, 1981). Under field conditions, in an area of high loading, the leaching of cations under the influence of sulphate has been observed. Sulphate anions supplied 76% of the electrical charge balance of the leaching solution through a coniferous soil in New Hampshire; in areas of low impingement, bicarbonate and organic anions dominate the anion composition (Cronan et al., 1978).

Mobilization of Trace Metals

A further by-product of increased soil acidity, and anion availability, appears to be the mobilization of certain metals, such as Al, Mn and Fe. At low concentration, Mn and Fe serve as essential nutrients for the growth of higher plants; however, there are some indications that, in excess, they can be detrimental to growth. Plant species vary in their susceptibility to certain metals. A case in point is aluminum, where differential responses to elevated levels have been demonstrated. Many factors affect tolerance/susceptibility, including soil pH, NH_4^+ versus NO_3^- nutrition, aluminum exclusion processes, Ca^{2+} and P nutrition, and organic-aluminum complexes (Foy et al., 1978). Plant species known to be sensitive to aluminum include barley, sugarbeet, corn and alfalfa.

The effects of increased metal mobilization may be more deleterious to aquatic life than to terrestrial vegetation communities. Experiments with soil in lysimeters (Abrahamsen et al., 1976) indicate increased loss of Al in relation to increased acid input. Substantial leaching of Al from soils into groundwater, then to streams and lakes, has been observed under field conditions in zones of very high impingement (Dickson, 1978).

Clay Transformations

Clay minerals are major inorganic components of soils, and the types of clay minerals generally found in soils are characteristic of parent materials and climate. Clay minerals have a considerable influence on physical, chemical and biological activities in many soils, because of their large surface area and structural characteristics.

Generally, the following conditions appear to be optimal for aluminum hydroxy interlayer formation: moderately active weathering to furnish Al ions, moderately acid pH, low organic matter, and frequent wetting and drying. An increase of precipitation acidity may, along with natural acidification, accelerate changes in clay transformation (Singh et al., 1981). The absence of direct evidence supporting or refuting such a hypothesis, however, precludes the drawing of conclusions concerning the likelihood that such acceleration is occurring under ambient loadings.

Influence on Soil Biota and on Soil Biochemistry

Laboratory experiments, or observations on soils in close proximity to pollutant sources, suggest changes which would occur in soil biota as a result of increased precipitation acidity (Singh et al., 1981). Observations indicate decreases in total numbers of soil bacteria and actinomycetes, and some relative increase in presence of fungi; although, under conditions of very high loading, fungi have been reported less abundant. Generally, total numbers of enchytraeids have not been affected (except under extreme conditions), though differential species responses have been reported (Abrahamsen et al., 1976 and 1977; Baath et al., 1980; Alexander, 1980).

The effect of acidity on soil respiration has not been conclusively demonstrated (Tamm et al., 1977; Rippon, 1980). However, increased acidification would seem clearly to diminish nitrate production, through its adverse impact on soil nitrifying bacteria. Particularly for NO_3^- preferring plants, change of soil pH could have a major effect on the overall N economy. Given the generally low N availability of many temperate and boreal region forest soils, such a mechanism could clearly control growth. However, sufficient evidence is not available at present to indicate whether ambient loads can effect sufficient change in soil pH to activate this mechanism.

Influence on Organic Cycle

Little information is available on this subject, but it would seem reasonable to separate the mixed biological/chemical decomposition processes of the forest floor from the essentially chemical transformations of the mineral horizons. Particularly in the boreal forest, decomposition is slow, and accumulation of organic matter is common. The forest floor is inhabited by large numbers of soil organisms; bacteria, actinomycetes, fungi, algae, viruses, protozoa, and various invertebrates, all of which take part in the breakdown of organic matter. Thus, observations made with regard to soil biology are relevant here.

The available evidence concerning the effect of acidity on organic breakdown is not conclusive. The weight of evidence from decomposition experiments, to date, suggests that acidification normally slows down organic matter decomposition. Moderate acidity tends to aggregate humic acid particles, but leads to dissolution and mobilization of fulvic acid. In soils, such as podzols, which contain appreciable concentrations of fulvic acid, substantial losses can occur in moderate acidic leaching. Low pH will favour the adsorption of fulvic acid on mineral surfaces, and will increase the adsorption of fulvic acid by expanded clay minerals. Under persistent acid conditions, both protons and solubilized fulvic acid will degrade minerals, and initiate other changes. Also of concern are the complexing and interactions of metalo-organic compounds and their mobility (Schnitzer, 1980). While good correlations seem to exist between such chemical relations and acidity, evidence is not available at present to indicate whether ambient loadings can produce sufficient change in soil pH to activate such mechanisms.

SENSITIVITY ASSESSMENT

Accelerated changes in the natural evolution of soils may occur as a result of an increase in the rate of acidification and subsequent nutrient impoverishment. These changes would hold important implications for long-term, sustained forest/agricultural productivity, and aquatic sensitivity. Recent discussions have indicated that the assessment of terrestrial sensitivity must consider and distinguish between those aspects of the terrestrial ecosystem which have an effect on forest and agricultural productivity, on the one hand, and aquatic sensitivity on the other (see Appendix I).

Implications for Forest Productivity

It is apparent that there are a number of factors that can interact with acid input to affect forest productivity (Morrison et al., 1981). The complexity of these factors requires the adoption of a more holistic, or ecosystem, approach to understanding this problem. A number of factors have now been defined, with their associated limits, for three levels of sensitivity in relation to forest productivity (Cowell et al., 1981). This information is presented in Table 4-5.

It is not implied that these are the only factors involved in determining terrestrial sensitivities as they relate to forest productivity; rather, they represent three of the more fundamental ecosystem characteristics which are measurable, and for which we can assign sensitivity criteria.

The main factor is soil chemistry, including exchangeable bases and SO_4^{2-} adsorption capacity. Other factors include soil depth and underlying materials.

Soil depth is defined as the weathered portion of the solum. Where the soil depth is less than 25 cm, the presence or absence of carbonate in the underlying materials, either parent material or bedrock, is considered. A soil depth of 25 cm is considered important because this is the zone of maximum root concentration and nutrient uptake. It also corresponds primarily with the organic and eluviated horizons of the profile. In addition, exchangeable base content is considered a better measure of sensitivity than CEC or pH alone.

SO_4^{2-} adsorption capacity is considered important for determining sensitivity, but, to date, little empirical data is available to establish limits.

TABLE 4-5. Forest Productivity Sensitivity

TERRESTRIAL FACTORS		SENSITIVITY		
		LOW	MODERATE	HIGH
Soil Chemistry				
i)	Exchangeable Bases	>15 meq/100g	6 to 15 meq/100g	<6 meq/100g
	Surrogate:			
	Combinations of pH in water (or % Base Saturation)	clayey, pH>5.0 loamy, pH>5.5 all calcareous soils	clayey, pH 4.5 to 5.0 loamy, pH 5.0 to 5.5 sandy, pH>5.5	clayey, pH<4.5 loamy, pH<5.0 sandy, pH<5.5
	AND Family Particle Size *OR* Texture	clay, silty clay, sandy clay (>35% clay)	silty clay loam, clay loam, sandy clay loam, silt loam, loam (10 to 35% clay)	silt, sandy loam loamy sand loamy sand, sand (<10% clay)
	OR CEC	>25 meq/100 g	10 to 25 meq/100 g	<10 meq/100 g
ii)	SO_4^{2-} Adsorption Capacity as determined by:	low organic matter *AND* high Al_2O_3 and/or $Fe_2O_3 + Fe_3O_4$		high organic matter *AND* low Al_2O_3 and/or $Fe_2O_3 + Fe_3O_4$
Soil Depth*				<25cm (10 to 12 inches)

* If soil <25 cm Underlying Material is incorporated

Underlying Material				
i)	Parent Material	carbonate bearing	non-carbonate bearing	non-carbonate bearing
ii)	Bedrock Material	limestone, dolomite, and metamorphic equivalents, calcareous clastic rocks, carbonate rocks interbedded with non-carbonate rocks	volcanic rocks, shales, greywacke, sandstones, ultramafic rocks, gabbro, mudstone, meta-equivalents	granite, granite gneiss, orthoquartzite, syenite

From Covell et al., 1981

In those soils which have a demonstrated capability for adsorbing sulphate to the soil sesquioxide surfaces (low organic matter, high Al_2O_3 and/or Fe_2O_3 + Fe_3O_4), the mobility of cations is reduced. Cations generally only appear in quantity in the leachates when sulphate moves through the profile. In terms of forest productivity it is assumed that extremely low pH soils (pH 4.0) are sensitive to acidification, even though the forest has reached equilibrium under low pH, low base conditions.

In this situation, any further loss of cations is considered significant, however small the loss may be. Basic to the determination of effects on forest productivity, however, is the assumption that the reduced availability of basic cations, because of replacement in the soil by H^+, is detrimental to forest growth. Only a few studies have been conducted which address this issue. Growth of red pine and other conifers has been shown to be limited by K^+ and Mg^{2+} deficiency in a restricted area of New York State (Heiberg and White, 1951; Leaf, 1968 and 1970; Stone, 1953), and in various parts of Quebec (Lafond, 1958; Swan, 1962; Gagnon, 1965).

In a small number of fertilizer field trials carried out with conifers in Canadian forests, P, K^+, Ca^{++} or Mg^{++} fertilizers did appear to elicit responses, though only when demand for N was first met (Foster and Morrison, 1981; Morrison et al., 1976, 1977a, 1977b). Forest mensuration studies, which have been directed to identifying linkages between acid precipitation and the growth of trees, have provided conflicting results (Morrison et al., 1981). Similarly, simulated acid rain studies conducted in Scandinavia have not yet established a direct cause/effect linkage.

In the case of nitrogen, acid deposition could have a beneficial effect on productivity, at least in the short term.

Despite this situation, any failure to establish relationships at present may only reflect an insensitivity of methods used, or, given the very wide range of forest and forest soil conditions versus the small number of studies, simply the lack of thorough investigation. The general restriction of commercial forest production to 'less productive' sites, coupled with new harvesting technology, where more of the tree is removed from the site, thus reducing the availability of nutrients for recycling, and the tradition of not applying lime, may increase the vulnerability of long term forest growth to acid precipitation.

Implications for Agricultural Productivity

Agricultural areas do not usually include the shallower soils that would be more sensitive to impacts from acid precipitation. The effects of fertilization and liming of agricultural soils generally will far exceed the direct effects of acid precipitation on the soil and thus make them essentially undetectable. In addition, acid precipitation could help offset sulphur deficiencies in some soils. The wide ranges in both soil properties and intensities of soil management result in a great variation in potential for significant effects on agricultural soils. However, the current state of knowledge suggests that the implications of air pollution for agricultural soils are that there will be minimal effects, even in those situations where greatest impact would be expected.

As for direct effects on crops, there is no conclusive documentation of effects occurring in the field, as a result of acid precipitation. However, experimental evidence does exist for a number of effects on crops, including the loss of nutrients from foliage by leaching, predisposition of plants to attack by pests, inhibition of nitrogen fixation, injury to plant surfaces, and reduced yield. Under experimental conditions, simulated acid rain of pH 4 or below has caused effects (see earlier discussion). However, great variation in sensitivity among species has been noted. The timing of acid precipitation events may be important in looking at effects on agricultural crops. What happens during the growing season is of primary concern, and within the growing season itself, there may be critical times. For a particular crop, there will be large areas at the same stage of growth at the same time. The significance of these relationships has not been determined, and further work is required before their significance will be understood.

Foliar injury and associated crop yield losses, resulting from ozone, continue to be a concern in agriculture. Significant effects can be expected in the most susceptible crops, from repeated exposure to ozone in excess of 0.08 ppm.

Terrestrial and Aquatic Environmental Linkages

Determination of the key terrestrial factors, which ultimately influence the impact of acid precipitation on aquatic ecosystems, involves a greater number of variables than those considered critical in assessing the sensitivity of forest productivity.

Special importance has been given to those variables which act to modify surface runoff and groundwater flow. Thus, in assessing the important linkages between the terrestrial and aquatic systems, additional emphasis has been placed on the more prominent role played by the whole solum and bedrock (Table 4-6). This approach assumes fairly simple basin flow conditions, in which much of the aquatic input (soil drainage) interacts with the soil body, and/or the bedrock surface.

Soil chemistry, soil depth, and bedrock type are factors common to assessing the sensitivity of forest productivity and the aquatic input sensitivity. As defined, they apply to regional evaluations more than

TABLE 4-6. Aquatic Input Sensitivity

	SENSITIVITY		
TERRESTRIAL FACTORS	LOW	MODERATE	HIGH
Soil Chemistry			
i) Exchangeable Bases	>15 meq/100g	6 to 15 meq/100g	<6 meq/100g
Surrogate:			
Combinations of pH in water (or % Base Saturation)	clayey, pH>5.0 loamy, pH>5.5 all calcareous soils	clayey, pH 4.5 to 5.0 loamy, pH 5.0 to 5.5 sandy, pH>5.5	clayey, pH<4.5 loamy, pH<5.0 sandy, pH<5.5
AND Family Particle Size OR Texture	clay, silty clay, sandy clay (>35% clay)	silty clay loam, clay loam, sandy clay loam, silt loam, loam (10 to 35% clay)	silt, sandy loam loamy sand loamy sand, sand (<10% clay)
OR CEC	>25 meq/100 g	10 to 25 meq/100 g	<10 meq/100 g
ii) SO_4^{2-} Adsorption Capacity as determined by:	low organic matter AND high Al_2O_3 and/or $Fe_2O_3 + Fe_3O_4$		high organic matter AND low Al_2O_3 and/or $Fe_2O_3 + Fe_3O_4$
Soil Depth	>1 m	25 cm to 1 m	<25 cm
Bedrock Geology	refer to Table 4.		
Soil Drainage	poor	imperfect to well	rapid
Landform Relief	level	rolling	steep
Vegetation	deciduous	mixed	coniferous
Vegetation Cover	continuous >60%	discontinuous to sparse 20 to 60%	very sparse to barren <20%

From Cowell et al., 1981

localized, site-specific evaluations (Tables 4-5 and 4-6). More critical limits and definitions will be applied as the scale of evaluation increases.

In terms of their influence on aquatic sensitivity, forest species appear to effect throughfall precipitation chemistry. There seems to be agreement that broadleaf, deciduous species, especially their leaf litter, provide more buffering of precipitation than coniferous species (Abrahamsen et al., 1976; Lee and Weber, 1980). This is the basis for rating vegetation in Table 4-6, but it obviously ignores acid contribution from snowfall and, to some degree, dry deposition.

Soil drainage refers to the rate at which the soil/rock body is drained, which in turn is related to porosity and permeability. Poor drainage does not necessarily imply an impermeable soil, rather, one of low hydraulic conductivity due to low permeability and/or high soil moisture (i.e. wetlands, gleysols, etc.). An impermeable surface (soil or rock) results in rapid surface runoff, with little opportunity for chemical equilibration, and, therefore, would be sensitive. Although rapidly drained soils are considered under high sensitivity, it should be noted that, in these conditions, there would also be less opportunity for drainage waters to leach significant concentrations of Al^{3+} into the aquatic system. Leaching of bases from forest soils would also be minimized.

It is intended that these factors will be used to assess sensitivities at a mapping scale of 1:1,000,000. Subsequently, larger scale evaluation of areas identified as having high sensitivity must consider additional factors to improve resolution. Probably the most important of these will be the hydrologic characteristics of individual watersheds. Generally, it has been found that upland headwater lakes and streams are especially susceptible to acidification (Morrsion et al., 1981). Also, the proportion of lake area to total drainage basin size is expected to influence pH changes. Thus, stream order and other drainage basin characteristics may be important determinants, when assessing sensitivities at larger scales.

The approaches proposed for assessing sensitivity must be considered only as a first approximation to identifying sensitive areas. Flexibility in approach will be necessary, until further scientific examination and mapping has been carried out.

The Ecodistrict data base for Canada and the Geoecology data base for the United States will allow evaluation of various combinations of these factors. They will also permit capability mapping, where each mapped unit (polygon or county) is assigned various sensitivity ratings, on the basis of different combinations of the factors which are shown in mapped format. This may also be a convenient method of standardizing the mapping format for the U.S. and Canada. Although the present data base is inadequate for mapping at a consistent scale across eastern North America, it will be useful to map, according to the level of information available, at the largest possible scale, using surrogates, as necessary, to estimate the factors outlined in Tables 4-5 and 4-6. At present, the best scale for portraying sensitivities for all of eastern North America is probably 1:1,000,000.

It is still premature to incorporate threshold loading (dose/effect) relationships into the sensitivity index. Much of what is known is based on laboratory simulation, or inconclusive field results, and awaits more rigorous testing. Loading factors are already incorporated into the base exchange ranges, because the limits chosen relate to the work of Wang and Coote, (1980). They assumed a loss by leaching of 25% of the exchangeable bases over 25 years, under an acid loading impact of 60 kg/ha $CaCO_3$ equivalent. In addition, it will be necessary to compare areas identified as sensitive to existing, measurable acid loadings. This may be carried out by calculating precipitation quantities over a specified period, weighted according to rainfall/snowfall event pH levels.

RESEARCH NEEDS

1. Improved system of mapping terrestrial sensitivity, incorporating such data bases as Geoecology and Ecodistrict (USA and Canada), to allow further identification of key sensitive areas.

2. An improved soils information base, including depth to carbonate, and sulphate adsorption capacity, in remote areas.

3. Relationships between forest productivity and acid sensitive properties of soils.

4. Better record of spatial and temporal measurements on impacts of acid precipitation (deposition data) in both the United States and Canada.

5. More vigorous field testing of hypothesis relative to impacts of LRTAP on forest productivity and water quality.

6. Projections of deposition of wet and dry materials, together with chemical composition, within well defined areas in eastern North America.

7. Field derived information, depicting changes in base status and nutrient availability on a representative variety of soils, in relation to deposition levels.

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SECTION 5

HEALTH AND VISIBILITY

INTRODUCTION

A complete assessment of the health implications of U.S./Canadian transboundary air pollution would encompass the full range of current pollution concerns, including photochemical oxidants, sulphur and nitrogen oxides, particulate matter, and associated toxic substances. Although future phases may address these air quality concerns, this report will focus on potential health effects associated with the transboundary deposition of acidifying substances.

Available information gives little cause for concern over direct health effects from acid deposition. The pH of acidic precipitation is generally well within the range normally tolerated by the skin and gastro-intestinal tract. Although high levels of SO_2, NO_2, and acid aerosols are reported in urban areas, no studies have been found that suggest adverse effects from dry deposition on the skin.

Evidence does suggest that inhalation of high levels of such substances may produce respiratory and other internal disease (EPA, 1980; NAS, 1978a), and one early epidemiological study (Gorham, 1958) even reported an (inverse) statistical association between bronchitis mortality and the pH of winter precipitation in Great Britain. In this case, precipitation acidity was probably an index of acid precursor air quality, since a plausible mechanism for causality does not exist.

Although a full discussion of the effects of direct inhalation of atmospheric acids is beyond the scope of this report, the circumstances in which inhalation of airborne acids might be implicated, as causative agents, are most likely to occur in areas of high pollution sources and population densities. The attribution of adverse health effects specifically to acid aerosols is complicated by the copresence of other pollutants, including particulate matter and photochemical oxidants.

Thus, the only health effects that may be associated with acidic deposition are indirect in nature. Based on the readily accessible literature, the two areas of most potential impact are: (1) contamination of edible fish by toxic materials, principally mercury; and (2) leaching and corrosion of watersheds, and water storage and distribution systems, leading to elevated toxic element levels in supplies of drinking water.

HEALTH

CONTAMINATION OF EDIBLE FISH

Some evidence suggests that acid deposition may alter the biogeochemical cycle of metals, including mercury (Tomlinson, 1978; Jensen and

Jernelov, 1972; Brosset and Svedung, 1977; Schindler et al., 1980). Poorly buffered waters in areas remote from any point source of discharge of mercury have been found to contain fish with elevated levels of mercury. Landner and Larson, (1972) first noted an inverse relationship between water pH and methyl mercury content of fish in certain Swedish lakes. Scheider et al., (1978) found that the mercury content of walleye from 21 Ontario Lakes was significantly higher for lakes where alkalinity was less than 15 mg/l (as $CaCO_3$), as opposed to lakes with higher alkalinities. According to Tomlinson, (1979), fish from poorly buffered lakes and rivers in Quebec, New Brunswick, Minnesota, New York, and Maine also contain elevated mercury.

The mechanisms by which acid deposition might increase fish mercury content are not known, but must likely involve both biological and chemical processes. The principal forms of mercury of interest are elemental (Hg^o), dimethyl mercury ($(CH_3)_2Hg$), mercuric mercury (Hg^{2+}), and monomethylmercury (CH_3Hg^+). Jensen and Jernelov, (1972), and several other investigators, have shown that inorganic mercury can be methylated in both aquatic and terrestrial ecosystems. One hypothesis, attempting to explain the relationship between pH and mercury, holds that monomethyl mercury formation is at low pH (<7), while dimethyl mercury forms at higher pH (>7) (Jensen and Jernelov, 1972; Tomlinson et al., 1979). Dimethyl mercury has a high vapour pressure, is relatively insoluble, and is thus largely released to the atmosphere. Methylmercury uptake by fish in lakes having these pH regimes is thus minimized. Lakes with lower pH produce proportionately larger amounts of monomethylmercury, which is efficiently taken up by biota. The reduced availability of young fish containing low mercury levels, and increased foraging activity by larger predator fish, both characteristic of acidified lakes, increase the bioaccumulation of methylmercury in larger fish. Recent experiments by Mayfield, (1980) found a very poor correlation between mono- and dimethyl mercury versus pH. The mechanisms leading to increased mercury burdens in fish are undoubtedly much more complicated, and probably include additional considerations, such as the complexity of the food chain, redox conditions, inorganic and organic requestering agents, watershed to lake area ratio (Sums et al., 1980), and rate of atmospheric mercury input. Using calculations from Brosset and Svedung (1977), Tomlinson et al., (1980) and Brouzes et al., (1977) it has been hypothesized that acid-containing clouds and rains should effectively remove methyl mercury from the atmosphere. The surface of acidified lakes should also be an effective sink for the dry deposition of methyl mercury. Once removed, methyl mercury would then be more likely to stay in solution in acidified waters. This scenario is shown in Figure 38, which illustrates the distribution of mercury in waters of three different acidities. Again, recent evidence suggests that the process is much more complicated (Barton et al., 1981). These authors could detect no dimethyl mercury in air from measurements taken at several locations in Ontario. Thus, while the exact mechanisms responsible for the observed elevated levels of mercury in fish from acidified lakes remain obscure, fish are harvested from these lakes, and

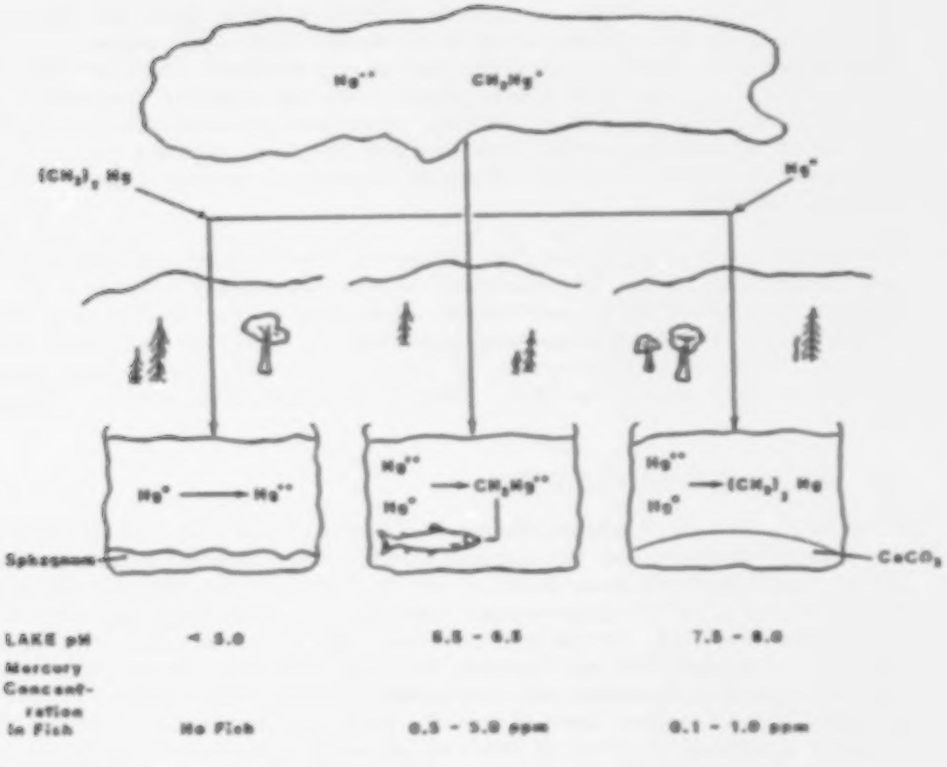
Hg^{++}
CH_3Hg^+
$(CH_3)_2Hg$
Hg^0
$Hg^0 \rightarrow Hg^{++}$
Hg^{++}
Hg^0
$\rightarrow CH_3Hg^{++}$
Hg^{++}
Hg^0
$\rightarrow (CH_3)_2Hg$
Sphagnum
$CaCO_3$
LAKE pH
< 5.0
5.5 - 6.5
7.5 - 8.0
Mercury Concentration in Fish
No Fish
0.5 - 5.0 ppm
0.1 - 1.0 ppm

Figure 38. Varying effects of lake pH on the distribution of mercury in ecosystems (Tomlinson, 1978).

present a potential health hazard to humans. The extent to which acid deposition may have contributed to mobilization, or retention, of mercury in fish, is speculative.

CONTAMINATION OF DRINKING WATER

Acid deposition can increase the concentration of toxic metals in drinking water by: (1) increasing the deposition of metal in soluble forms (e.g. mercury); (2) leaching of metals from the watershed and from sediments; and (3) acid corrosion of materials used in reservoirs and drinking water distribution systems.

Again, no clear evidence of health effects arising from the consumption of drinking water, contaminated with metals from acid deposition, have been reported in the literature; but some potential problems have been identified. In New York State, water from the Hinkley reservoir has become acidified to such an extent, that lead concentrations in drinking water at the top exceed the maximum levels for human use, (50 µg/l) recommended by the New York State Department of Health (Turk and Peters, 1977).

Groundwater may also become acidified in poorly buffered areas (Cronan and Schofield, 1979); for example, it has been reported that, in Sweden, some well water has become acidified to the extent that substantial corrosion of household plumbing has occurred (Holtburg and Wenblad, 1980). An occurrence of this kind could lead to increased levels of such metals as zinc, copper, lead and cadmium in drinking water.

Groundwater Quality in Ontario

Many wells in the Precambrian area of Ontario are located in proximity to shallow bedrock, so the potential for acidification exists. The first field surveys were carried out in 1980 in the Muskoka-Haliburton area. A total of 85 groundwater samples were field-tested, and 28 samples were analyzed, for major ions and some trace metals, in the laboratory. Groundwater was sampled in July from shallow springs and wells, from both bedrock and overburden formations. Eleven of the 85 samples had pH values less that 6.0, with the lowest value being 5.2. October sampling of five of the low pH wells resulted in only one sample with a pH value less than 6.0, suggesting that groundwater pH may fluctuate during the year. The lowest recorded pH of 5.2 was from a shallow well, servicing a permanent home near Bracebridge, Ontario. The owner has lived there about 10 years but during the last three years has experienced water supply equipment failure, which has been attributed to acidic water reaching the system.

Altered Groundwater Chemistry in the Adirondack Region

The New York Department of Health has undertaken studies of acid precipitation effects on drinking water in the Adirondack Mountains of New York State. They have concluded that acid precipitation in the Adirondack region of New York is affecting the quality of drinking water, to such an extent that violations of drinking water standards could occur. In spring waters, the leaching of metals from natural bedrock or overburden can produce elevated metal concentrations. High concentrations are found in homes using metal piping in their distribution system, particularly if the lines are used intermittently.

Sharpe et al., (1980) provide significant information on the effects of deposition of lead and cadmium, as well as acid deposition, on the quality of drinking water from cisterns in Clarion County, PA. Wet and dry deposition of lead and cadmium resulted in solutions that were in the same order of magnitude as recommended United States drinking water limits (50 μg/l and 10 μg/l respectively). Lead levels in tap water from cisterns were much higher than those found in the source water; about 16% of the households sampled had tap water levels in excess of the United States drinking water standard. The investigators concluded that the increase in tap water lead levels resulted from acid corrosion of the lead solder in the joints in the cistern and plumbing. Thus, cistern water users are at special risk in areas of high acid deposition.

There is a time dependence for the initiation of adverse health effects resulting from drinking water contaminated with metals at, or approaching, the concentrations listed in Table 5-1. For example, brief episodic excursions of lead over the recommended standard, associated with snowmelt derived acidity in water from small lakes or streams, is not likely to be of major concern. Longer or continual consumption of water containing lead levels 25μg/L could be of concern (NAS, 1977), although the actual standard for drinking water lead levels in the United States and Canada is 50μg/L.

SENSITIVE AREAS AND POPULATIONS

Areas

In summary, the following areas will be particularly sensitive to health hazards from contaminated fish and drinking water:

1. poorly buffered lakes and streams (with a viable fish population);
2. watersheds with unusual accumulations of metals in sediments or soils;
3. areas that lack drinking water treatment facilities; and
4. areas with substantial lead plumbing.

TABLE 5-1

CANADIAN AND UNITED STATES DRINKING WATER GUIDELINES FOR TOXIC METALS (µg/L)

	Canadian	United States
Lead	50	50
Mercury	1	2
Cadmium	5	10
Copper	1000	1000
Zinc	5000	5000
Arsenic	50	50
Selenium	10	10

The ability to define, monitor, model, and control anthropogenic visibility impairment is dependent on current scientific and technical understanding of the factors that affect atmospheric visibility. Because visibility involves the human perception of the physical environment, evaluation of the effects of air pollution on visibility must include specification of the process of human visual perception, and quantification of the impact of air pollution on the optical characteristics of the atmosphere.

From a scientific and technical point of view, deterioration of visual air quality is probably the best understood, and most readily measured, effect of air pollution. However, many important uncertainties and limitations exist in available knowledge. Significant implications of current understanding of vision in the atmosphere may be summarized as follows (EPA, 1979).

(1) Visibility impairment is caused by the scattering and absorption of light by suspended particles and gases. Fine solid or liquid particles (atmospheric aerosols) and, to a lesser extent, nitrogen dioxide, are the most important anthropogenic causes of degraded visual air quality. Air molecules, weather variables and natural emissions also effect visibility.

(2) Light scattering and light absorbing pollutants reduce the amount of light received from viewed objects, and scatter ambient or 'air' light into the line of sight. This scattered air light is perceived as haze. Because these effects vary with the wavelength of light, discolouration can result. Extinction (b_{ext}) is a measure of light scattering and absorption.

(3) These effects can be quantified or approximated through use of theoretical mathematical treatments and experimentally derived pollutant/optics relationships.

(4) The perceptibility of pollution effects on light depends on human eye/brain responses. Studies of the eye/brain response to contrast indicate that typical observers can detect a 0.02 (2%) or greater contrast between large, dark objects and the horizon sky. Assuming this threshold contrast, visual range, the farthest distance at which a large black object can be seen against the sky, is related to extinction by the Koschmeider equation:

$$Vr = \frac{3.9}{b_{ext}}$$

Populations

The following populations will be susceptible to health hazards resulting indirectly from atmospheric deposition:

1. those dependent on fish from acidifed waters as a major dietary staple;
2. those with elevated mercury or lead blood levels from other exposures;
3. women of childbearing age, and children;
4. those dependent on cisterns as a primary source of drinking water.

DATA NEEDS AND RESEARCH REQUIREMENTS

Work is required to delineate the following factors, related to the effects of acid deposition on human health:

1. levels and species of metals in edible fish in the U.S.A. and Canada;
2. levels and species of metals in drinking waters of the U.S.A. and Canada;
3. levels of human tolerance for mercury in fish;
4. data to more fully characterize and identify sensitive areas and receptors;
5. deposition rates of acid from acidic precursors, such as sulphur and nitrogen oxides;
6. effects on health from episodic and long-term exposures to acidic pollutants in most sensitive receptors.

VISIBILITY

IDENTIFICATION OF KEY EFFECTS ON VISIBILITY

The effect of transboundary pollution on visibility is directly related to air quality, rather than deposition. The particulate phase precursors to acid deposition (mostly sulphuric acid aerosol and various ammonium sulphate aerosols) play a major role in atmospheric visibility. Available data suggest that nitrates exist predominantly in the vapour phase, and are, for the most part, of little consequence to visibility in eastern North America. However, for isolated point sources, visible brown plumes from NO_2 have been reported at distances of 100 km from the source (Menlo, 1980).

The overall impact of aerosol haze is to reduce visual range and contrast, and to change colour. Visually, the objects are 'flattened', and the aesthetic value of a vista can be degraded, even though the distances are small relative to the visual range. Much of the scenic value of a vista can be lost, when the visual range is reduced to a distance that is several times the greatest line-of-sight range in the scene (Charlson et al., 1978).

Aerosol haze can also degrade the view of the night sky. Star brightness is diminished by light scattering and absorption. Perception of stars is also reduced by an increase in the brightness of the night sky, caused by scattering of available light. In or near urban areas, night sky brightness is significantly increased by particle scattering of artificial light. The combination of extinction of starlight and increased sky brightness markedly decreased the number of stars visible in the night sky at fine particle concentrations of 10-30 $\mu g/m^3$ (Leonard et al., 1977).

As noted above, available empirical information suggests that fine particulate sulphates play a major role in visibility reduction. Direct measurements and statistical analyses indicate that fine sulphate aerosols account for 30-60% of visibility reduction, related to fine particles, in areas as diverse as the northeastern United States, Los Angeles and the southwest Mountain States. However, other fine particle constituents are also important, and can dominate light scattering and absorption in various regions (EPA, 1979).

Studies of trends in eastern U.S. airport visibility indicate that, while winter visibilities improved in some northeastern locations, overall eastern visibility declined. Summer, often the season of best visibility in the early 50s, currently provides the worst. From 1948 to 1974, summertime haze (extinction) increased by more than 100% in the central eastern states, by 50-70% in the Midwest and the eastern Sunbelt States, and by 10-20% in the New England area. Although the results of airport surveys should be viewed with caution, the results are consistent from site to site (Figure 39).

Comparable data should be available soon for eastern Canada (Husar et al., 1979).

Very close parallels have been noted between the geographical/seasonal features of airport visibility trends, and the geographical/seasonal features of trends in atmospheric sulphate concentrations, sulphur dioxide emissions, and coal use patterns. These parallels provide strong circumstantial evidence that the historical visibility changes in the east were caused, at least in part, by trends in sulphate concentrations and sulphur dioxide emissions.

Episodes of regional scale haziness have been observed, in the eastern United States and Canada. Examination of airport data, pollution

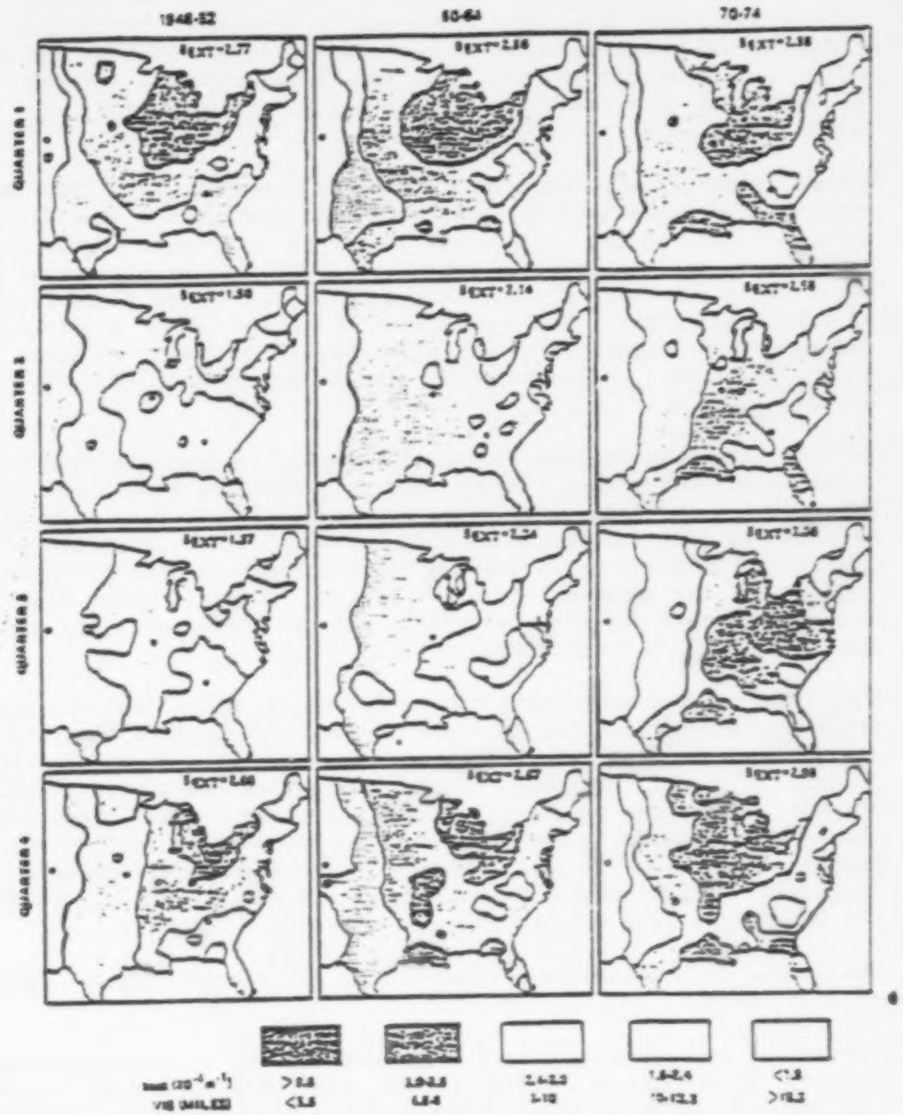
1948-52
60-64
70-74
QUARTER 1
QUARTER 2
QUARTER 3
QUARTER 4
VIS (MILES)

Figure 39. Seasonal and spatial distribution of long-term trends in average airport visibilities for the eastern United States (Husar et al., 1979).

measurements and satellite photography indicates that these haze air masses move across eastern North America in the manner of high pressure systems, causing significant visibility reductions in areas with little or no air pollutant emissions.

ASSESSMENT OF IMPACTS

As noted above, visibility in the northeastern U.S. and Canada shows strong seasonal trends, with periodic episodes of intense haze moving across large regions several times each summer. In addition to the obvious adverse aesthetic effects, when fine particles and humidity combine to reduce visual range below three miles, aircraft operations are curtailed.

Figure 40 illustrates the relationship between fine particle loadings and visual range. At high background loadings, small increments make only small changes in visibility. Humidity strongly enhances the effects of fine sulphates, as shown in Figure 41. This relationship, is derived from regressions of form:

$$b_{ext} = b_o + \frac{0.04\ (\text{sulphate})}{(1 - \text{RH})}$$

When background conditions are understood, this can be used to relate predicted sulphate levels to resulting visual range. On the other hand, actual impacts must be derived from the results of regional modelling runs.

SENSITIVE AREAS AND POPULATIONS

Clean areas such as found in western North Aermica, are the most sensitive to visibility degradation. In the U.S., the Clean Air Act affords special protection to visibility in 156 'Class I' areas, including national parks and wilderness areas. Many of these Class I areas are located near the U.S./Canadian border and one (Roosevelt-Campobello) in Canada. However, any area, urban or rural, with normal viewing distances of a mile or more may be affected by episodic regional haze, carrying acid precursor substances.

Assessment of the relative value of visibility in urban, versus rural, areas is beyond the scope of this report.

DATA NEEDS/RESEARCH REQUIREMENTS

The following instruments are required to complete work related to the effects of atmospheric deposition on visibility:

1. output of regional modelling groups;
2. decision on how to treat aesthetic effects of long-term transport of air pollutants.

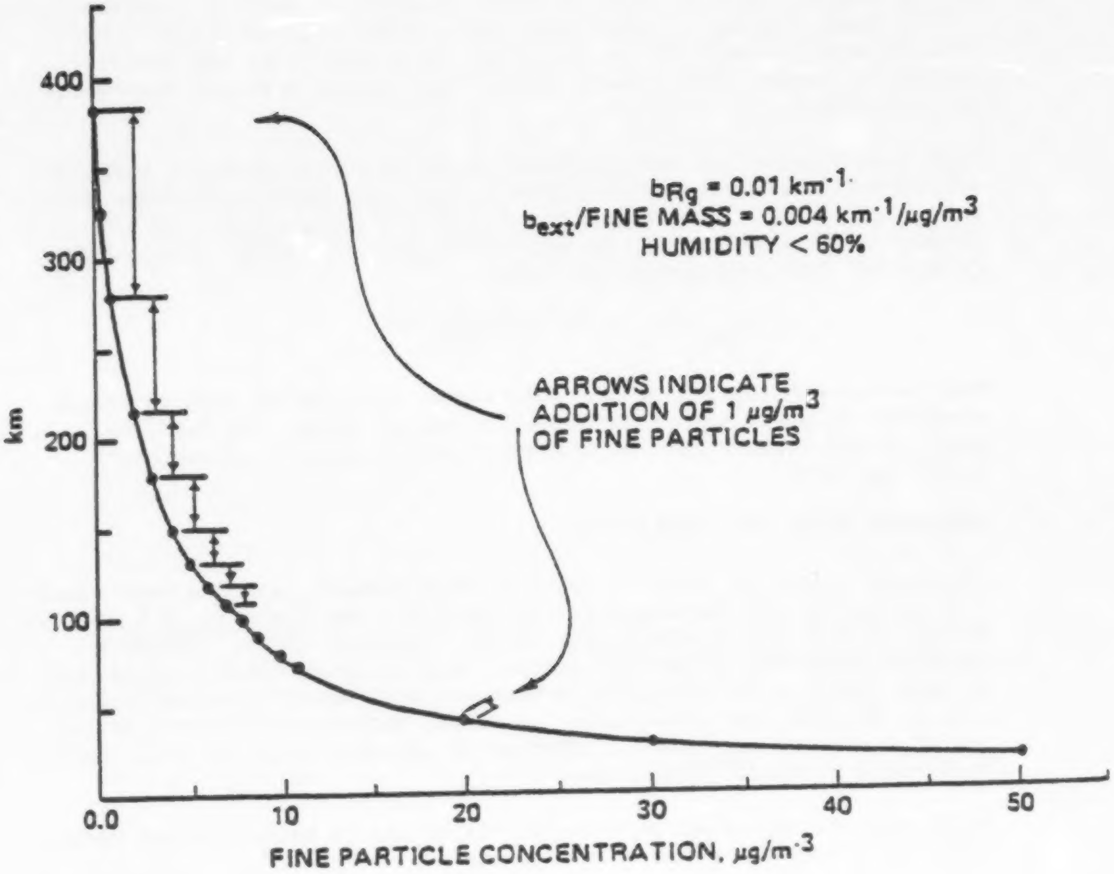

Figure 40. Effects of fine particle increments on calculated visual range (EPA, 1979).

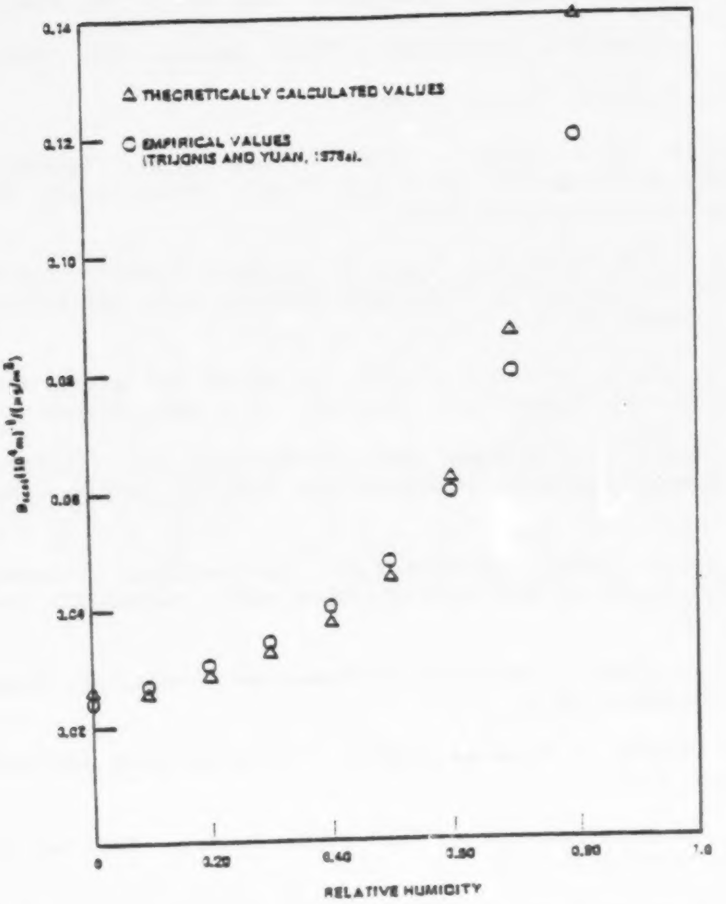

Figure 41. Light-scattering per unit mass of sulphate aerosol as a function of relative humidity (Latimer et al., 1978).

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SECTION 6

EFFECTS ON MAN-MADE STRUCTURES

INTRODUCTION

The following general comments on the impact of acid precipitation are drawn from a number of sources in the literature, which are discussed more completely in subsequent sections. It must be pointed out here that many of the studies referred to are somewhat qualitative, owing to the lack of simultaneous corrosion measurements and air quality and acidic deposition monitoring. As a result, while many of these studies have proven an effect, a comprehensive assessment of economic implications is not available at this time.

Acid deposition, oxidants, gases and particulates contribute to the accelerated degradation of materials. Plastics, elastomers, and organic paints and coatings are degraded by oxidation and by acid-catalyzed polymer decomposition. Particulates adversely affect the appearance of surfaces and can cause retention of aggressive chemical species on the surface. Particulates that contain iron or calcium carbonate can create local electrochemical cells of high activity.

Many typical metallic construction materials are adversely affected by acid deposition, through increased dissolution of protective surface surface oxides, or of the metal itself. Oxidants are thought to be less damaging to metals, and, in some cases, have been shown to lower metallic corrosion rates. Certain specialized metallic electronic components have been shown to be very sensitive to certain pollutants, particularly SO_x species.

Masonry materials exhibit a wide range of responses to pollutants. Carbonate-containing materials, such as limestone or marble, are very susceptible to attack by acid deposition. Recent studies have shown that these materials can be attacked by atmospheric sulphur dioxides through several mechanisms. The oxidation of sulphur dioxide to sulphuric acid can be catalyzed by chemical means (metallic ions, particularly Fe^{2+}, or carbon), or by microorganisms. The sulphate ion reacts with the calcium carbonate of the stone, to form calcium sulphate (gypsum) (Fassina et al., 1976). Also, bacterial reactions with granite have been observed. Regarding microorganisms, other bacteria can act in a similar manner, converting atmospheric ammonia to nitric acid, while the carbonate in the stone is converted to water-soluble nitrate compounds.

Other masonry materials, particularly those containing large amounts of silicates (e.g. concrete), are more resistant to most acidic atmospheric pollutants. However, reinforcing steels within concrete may be susceptible to attack. Wood materials in construction are generally resistant to weak acid deposition, but are known to be attacked by oxidants.

As the effects of air pollutants on materials become better understood, it will be possible to perform cost/benefit analyses, and to develop policy guidelines relating to the amounts of pollutant loading that can be tolerated, from an economic point of view. Some attempts have already been made in this direction. However, as is the case for degradation occurring in pristine wilderness areas which are ecologically sensitive, it is not always possible to provide an objective economic assessment of damage to man-made structures.

It is recognized that the architectural and sculptural expressions of our two heritages are a non-renewable resource of the most precious sort. Historic structures and monumental statuary represent the most visible aspects of historical and cultural evolution. In the United States, legislative recognition of the value of this cultural heritage, mandating its preservation, began in 1906, with the passage of the Antiquities Act, and continues to this day, with the passage of the National Historic Preservation Act Amendments of 1980. The 1916 Organic legislation of the National Park Service mandates the conservation of "...'historic objects'...to provide for the enjoyment of the same in such a manner and by such means as will leave them unimpaired for the enjoyment of future generations."

In Canada, similar legislative action has been taken in the Archeological Sites Protection Act, and in the 1953 Historic Sites and Monuments Act.

Preservation of original material or fabric is intrinsic to maintaining the cultural value of architectural and sculptural works. The patina of history cannot be replicated; natural materials incorporated into man-made structures cannot, in most cases, be duplicated today, and, in any case, are subject to replacement in cost/benefit analytical terms. The sources of supply for historic building materials are limited, if not extinct. Quarries have been exhausted, and stands of first growth timber are scarce. The pool of skilled craftsmen and artisans, able to extract and shape these materials, is diminishing. Most importantly, perhaps, historical associations with original fabrics are irreplaceable. As in the case of many sensitive ecological systems which are being altered, degradation of certain man-made structures is an irreversible process. For these reasons, the monuments of our cultures must be distinguished from natural and economic resources, in studying the effects of atmospheric depositions. Scales for measuring the net loss of deterioration must embrace aesthetic and historical contributions. Trade-offs made in mitigating the impact of air pollutants must address the preservation of the qualities that constitute the significance of the monument. Notwithstanding these qualifications, it is possible to make reference to economic assessments of corrosion damage attributed to air pollutants. A recent study completed by the Council for Environmental Quality has estimated that the cost of damage, due to corrosion of buildings and structures in the United States is of the order of $2 billion per year. Damages to natural ecosystems, crops, etc. are additional. This $2 billion cost does not differentiate, however, between local effects and effects due to pollutants which have been transported from distant emitters.

A second report, released by the OECD, indicates that for a 50% reduction in SO_2 emissions, based on an expected production of 24.4 million metric tons in 1985 (11 European countries), the resulting benefit, in terms of reduced damage, would be of the order of $1.16 billion per year. In this case, the benefit is based on corrosion of metals only, and excludes limestone and sandstone structures, since no exact dose/response relationships are available between deposition of sulphur compounds on these materials and corrosion rates. This cost does not distinguish between different sulfur species, such as sulphuric acid in acid rain, or SO_2. Nor is the loss due to impoverishment of a cultural heritage assessed.

ASSESSMENT OF EFFECTS

Any assessment of the impacts of atmospheric pollutants on man-made structures must take into consideration several complicating factors. To start with, not all building materials are durable, even in the absence of atmospheric deposition. Hence, it is important to differentiate between expected weathering, and accelerated deterioration attributable to deposition. To date, there have been virtually no studies which provide estimates of the relationship between degrees of deterioration and atmospheric deposition, the so-called dose-response relationship. Monitoring of air quality indices, of meteorological phenomena, and of local environments in areas where accelerated deterioration occurs, has been scanty. The taxonomy for describing and measuring the deterioration of metal, architectural, and sculptural materials is not yet universally accepted.

A further complicating feature, in assessing damage related to acidic precipitation and pollutants carried from great distances, is the confounding impact of local pollution sources. In the case of sulphur dioxide, the conversion rate to sulphate in the atmosphere is slow, of the order of 3% per hour. If local SO_2 emissions are deposited on local buildings, and are subsequently oxidized to sulphate, it is impossible to distinguish the local source of secondary sulphate from the sulphate deposited by acidic precipitation, and having originated at a source several hundred kilometers upwind. Therefore, if we are to assess the impacts of long-range transport of air pollutants, such as occur during transboundary flow, we must try to determine the additional effect of these pollutants on deterioration processes, which are already occurring, as a consequence of local emissions. This task is possible at those sites where local emissions are very small, but is normally extremely difficult in large urban centers. It should be noted, in addition, that local corrosive effects of the primary pollutants (e.g. SO_2) are fairly well documented, while the role of acidic precipitation in corrosion processes is not well understood.

The primary species involved in the deterioration of man-made structures include SO_2, H_2SO_4, O_3, NO_x, HNO_3, CO_2, Cl^-, $CaCO_3$, iron and soot. In addition, there is evidence suggesting an indirect effect due to ammonia. It is understood that the pollutants may be delivered to the corrosion site in either wet or dry form, that is, during a precipitation event, or during a dry period. The dry deposition may occur in particulate or gaseous form.

MECHANISMS

Chemical/physical corrosion processes are those most extensively discussed in the literature. It is suggested that SO_2 is the primary species causing damage to materials exposed to the atmosphere (Kucera, 1976; Mikhailovskii and Sanko, 1979; OECD, 1979). Corrosion rates of metals are particularly high in urban areas, and, as a result, might be associated with local emissions of SO_2. On the other hand, the impact of acidic precipitation is not well understood. The pH value of precipitation is probably a significant factor in the case of zinc and copper, which develop protective coatings of basic carbonates or oxides (Guttman and Sereda, 1968; Mattsson and Holm, 1968). At pH near 4, the protective coating may be rapidly dissolved, exposing the metal (Allaino-Rossetti and Narabelli, 1976; Gettens, 1964). The dry deposition of sulphates is potentially a source of acidic solution, once water is available at the surface. Hence, all dry materials that have fallen upon a surface during a dry period may directly cause corrosion, or may lead to enhanced corrosion, once a surface is wetted.

There is little information relating corrosion rate and available NO_x. However, HNO_3 has a very deleterious effect on most metals, more so than H_2SO_4 or HCl (McLeod and Rogers, 1968). In addition, metal nitrate salts tend to be more soluble than the sulphate salts, which means that nitrate corrosion products could be readily washed from surfaces, exposing fresh metal to attack, while sulphate products could remain on the surface to inhibit further corrosion. Also, when the corrosion products are washed onto masonry surfaces, very damaging efflorescence can occur.

The implications of HNO_3 corrosion are serious, when taken in the context of NO_x emissions predicted for the next 20 years. It is expected that these will increase significantly (McBean and Altshuller, 1980). The conversion of NO_x to nitric acid, during its residence in the atmosphere, is not well understood, but more and more attention is now being focused on nitrogen chemistry and its contribution to acidic precipitation. Should the nitric acid in the rain be deposited with chloride-containing species, the corrosive potential is greatly increased.

There is evidence to suggest that ozone reduces the corrosion of many materials, except for organics, such as paint and plastics (Haynie and Upham, 1971; Haynie et al., 1976; Spence and Haynie, 1972).

Considerable work is currently underway to examine the processes involved in the deterioration of natural masonry materials, such as limestone, marble and sandstone. In all cases, the stone provides varying amounts of calcium carbonate; acidic water reacts with the available calcium carbonate to form gypsum ($CaSO_4$). Other sulphates, such as Na_2SO_4, are also formed. These sulphates are very soluble materials. In the case where $CaSO_4$ is formed on sandstone, the high porosity of the sandstone provides an open structure for the internal development of gypsum crystals, which exert extremely large pressures in the porous stone, and lead to internal disintegration (Arnold, 1976; Braun and Wilson, 1970; Spedding, 1969; Thompson and White, 1974; Weaver, 1980). Since the gypsum in solution can migrate over the total surface of a sandstone building, it is possible for deterioration to occur everywhere, not just at the site where acidic water struck the building material. The surface dissolution of limestone and marble, and the further dissolving of mortar between building stones, can lead to both deterioration of the surface and weakening of the structure, owing to the leaching of mortar.

Other salts may form through the process of efflorescence, and, under freeze-thaw conditions, cause spalling within the lattice of the surface and subsurface strata.

There is little information on the effects of atmospheric ammonia on the corrosion of materials. However, it has been suggested that ammonia may be a major indirect contributor to the early stages of atmospheric corrosion (Ross and Gallaghan, 1966). Ammonia reacts with water to form ammonia hydroxide, which has a lower surface tension than water. In consequence, a larger portion of the material surface can be wetted, and become, therefore, more susceptible to attack by atmospheric pollutants.

Biological weathering recently has been proposed as a major contributor to deterioration. Bacteria on the surface of buildings draw sulphur dioxide (SO_2) from the atmosphere; the microbe's metabolic system converts the gas into sulphuric acid, which it uses as a digestive fluid (Babick and Stotzky, 1978; Hansen, 1980). The digestive fluid attacks the calcium carbonate in stone, and liberates carbon dioxide, the microbe nutrient. At the same time, the stone is converted into calcium sulphate. Similar distructive reactions can occur on granite, where carbonate-containing dust can support the initial reactions. Once initiated, bacterial action can attack the granite silicate structure (Winkler, 1973).

Processes that might occur subsequently are similar to those discussed in the previous section. Essentially, biological activity differs from chemical/physical corrosion, in so far as, in the first case, the SO_2 is used directly by the microbe to produce an acid whereas, in the second, the SO_2 has to be chemically oxidized to sulphate.

The unexpected existence of microbiol activity in an oxygen atmosphere has been explained in terms of surface incrustations. Soluble reaction products can remain deposited on the surface to further react with ions from the substrate, or other depositions, to form coherent incrustations. The black crust, or scab, on Venetian monuments has been shown to contain recrystallized calcite, an insoluble cement for gypsum and carbon particles (Fassina et al., 1976). Incrustations can create a shield behind which an intensively aggressive microenvironment exists, where further deterioration can take place.

Examination of microbial communities on structures throughout the world is currently underway. In many cases, the microbe seeks a substrate which contains carbonate material. Other bacteria can act in a similar manner, converting atmospheric ammonia to nitric acid, and causing the carbonate in the stone to be replaced by water- soluble nitrate components, or to be dissolved by the acidic environment.

IMPLICATIONS OF TRENDS

It is anticipated that, over the next 20 years, NO_x emissions into the atmosphere will increase in the order of 35%. During the same period, it is expected that SO_2 emissions will remain the same, or increase slightly, based on current energy utilization projections. Under these circumstances, it is anticipated that the nitric acid in rain will substantially increase, with large potential effects in terms of materials deterioration, in particular when chloride ions are present.

Since the pollutants causing corrosion and deterioration may be delivered to the material in either wet or dry form, it is of interest to examine the consequences of periodicity. It has been shown that, in some instances where most of the deposition occurs in dry form, the occurrence of rain may, in fact, be beneficial, even if the rain is acidic, since it performs a washing function, removing the collected deposition of corrosive materials from previously dry surfaces. In the event that the site receives regular acidic rain, it is the wet deposition which delivers the main corrosive load to the materials site.

Hence, it is both the chemistry of the material being deposited, and the episodicity of deposition, which must be taken into consideration in assessing the potential for damage. In this regard, it is of interest to consider the consequences of a light shower of acidic precipitation falling upon painted metal. Should the shower be followed by a sunny interval, it is possible that the metal surfaces may heat up quickly, and at the same time be covered with small droplets (micropools) of acidic water, which are evaporating. This combination of events may produce serious corrosion damage to the painted surface.

Another example of episodicity is the occurrence of spring snowmelt after a subzero period of many months. In this case, all the pollutants delivered, either by the snow or in dry form, are available for dissolution from the snow pack. Since most of the pollutants are selectively leached from the pack with the first 10-15% of melt water, the resulting fluid could be very corrosive. If the snow has been accumulating on buildings, or if surface runoff flows down the sides of foundations, considerable damage may result.

SUSCEPTIBLE MATERIALS AND THEIR DISTRIBUTION

All types of man-made structures show some sensitivity to air pollution. Metals are most affected by acidic species which can cause dissolution of the metal or protective surface films. Organic materials, that is, plastics, paints, elastomers, and wood, are attacked by acids and oxidants (Spence, 1972). Masonry materials are affected by acids and, indirectly, by bacterial growth that depends on the availability of pollutants, such as SO_2.

Several cases of specific damage to masonry structures at well documented sites are noted in the literature.

1. The Elgin Marbles, transported to the British Museum at the end of the 18th Century, can be viewed as a control group for measuring atmospheric effects on the buildings of the Acropolis in Athens, Greece (Skonlikidis et al., 1976; Spence and Haynie, 1972). The impeccable state of preservation of the marbles contrasts sharply with the sculptures which, until recently, remained in situ.

2. The Cathedral in Cologne, West Germany, has suffered much deterioration from its urban-industrial environment (Luckat, 1976; Seneviratne, 1976). In contrast, Ludwig II's Neuschwanstein Castle, built of stone from the same quarry at the same time that Cologne Cathedral's 200-year building program was completed, offers a real-world controlled sample. The stone at Neuschwanstein shows no sign of deterioration, in contrast to the crumbling stone of the Cathedral. Atmospheric sulphate decomposition at Neuschwanstein measures 6-8 mg/m^2/day compared to 130 mg/m^2/day in the Cathedral area. In both cases, however, it should be noted that the exposed, deteriorated structures are being subjected to extremely high local levels of pollution.

3. A recent study in Ottawa, Canada, has documented the consequences of both material dissolution and internal fracturing of sandstone buildings (Weaver, 1980). In this instance, substantial deterioration is probably less a consequence of local pollution than of pollution carried from long distances. However, acid deposition is causing release of pollutants trapped in the stone in past years, causing increased damage. Ottawa is essentially a non- industrial city, but its rain has an annual average pH of less than 4.5.

4. The American Environmental Protection Agency has a study underway to assess the effect of acid rain on marble and granite gravestones, marking military graves in the United States (Baer, 1980). These stones, provided by the Veterans Administration, are obtained from only two or three quarries, and have been placed in over 100 national cemeteries throughout the country, since veterans first were eligible to receive them (1873). The stones provide two sets of chemically uniform indicators (granite, marble), which have recorded, over precise periods of time, the effects of corrosion at each site.

Bronze statuary is another case where major concern is focused on the maintenance of a tangible heritage, which is being subjected to the effects of atmospheric deposition. As is the case with buildings, the distribution is concentrated essentially in urban centers. The sculptured shape is the key value, rather than the structural material itself; corrosion of the sculptured surface is tantamount to loss of the cultural value of the statue.

Protective coatings applied to both monuments and buildings are treated as sacrificial finishes. If weathering of the finish or coating accelerates with increased pollutant deposition, then the cycle for renewal can be adjusted. At present, however, sacrificial coatings for masonry structures are not viable. Attempts to shield threatened masonry structures with protective coatings have not generally been successful; they are subject to failure in adhesion, and often cause spalling of the substrata material. With regard to statuary, coatings must not only meet corrosion requirements, but also maintain aesthetic qualities.

As noted, the great majority of buildings, structures and statuary, which are being subjected to the deteriorating process associated with atmospheric transport and deposition, are found in urban areas. Hence, a delineation of sensitive areas does not take into consideration geographic features, but, rather, industrial and demographic distribution. As mentioned above, the assessment of deterioration, due to pollutants transported over long distances, is confounded by the impact of pollution produced locally. For instance, in northern climates, corrosive effects due to atmospheric pollution may be totally masked, in winter, by the impact of road salt ($CaCl_2$ and/or NaCl), which is particularly corrosive to metals. These salts can also damage porous masonry building components, through mechanisms similar to those discussed earlier for gypsum.

DATA NEEDS AND RESEARCH REQUIREMENTS

Although examination of the corrosion of materials is a well established discipline, the dose-response relationship between atmospheric pollutants and material corrosion is rather poorly documented. Some gross relationships are understood, but appreciation of the influence of micro-environmental parameters, such as surface variation and structural shielding from exposure, is at the nascent stage.

Work is required to delineate the following specific factors:

1. deposition ingredients which are active on selective materials (e.g. the impact of ammonia on the corrosion of metal);
2. effect of constant background levels of chloride ions on the corrosion of materials;
3. the role of particulates in materials degradation;
4. the role of sulphate ion in the corrosion of materials compared to the important role of SO_2;
5. effects of episodic and continuous moisture and temperature cycles;
6. effects of biological activity, particularly on building materials containing carbonate species, or on surfaces exposed to carbonate-containing dusts.
7. neutralizing agents which may be available, and which have not yet been monitored in precipitation network studies;
8. dose-response relationships for a range of corrosive agents and surfaces, determined in field and controlled environments, and in laboratory models;
9. the relative importance of wet- and dry-deposit pollution in the subsequent corrosion process.
10. the role of electrostatic effects produced in porous stone by the absorption of strong electrolyte solutions.

In addition to these areas of study, which have not yet been adequately addressed, there are certain data sets which would be useful in the development of a final report:

1. estimates of wet and dry chloride deposition (since chloride plays a very important synergistic role, with nitric and sulphuric acid, in corrosion processes);
2. estimates of pollutant loads on susceptible structures, giving relative contributions by local sources and distant sources;
3. data from the EPA tombstone study, which is now underway in the United States.

METHODOLOGIES

Testing materials to determine their resistance to corrosion, or degradation in the atmosphere, is conducted at a number of established sites around the world. Approximately 15 of these sites are in the United States, east of the 100th meridian, with additional sites being maintained on a proprietary basis by individual organizations. The sites are typically characterized as rural, urban, industrial, or marine to reflect the perceived quality of the environment at each site. Meteorological and air quality monitoring have not generally been performed at these sites. Recently, measurements of temperature, rainfall, humidity, wind speed and direction, solar radiation, SO_2 and chloride ion concentration, were begun at the Kure Beach, North Carolina, marine site. There is no evidence that measurements of acid deposition, nitrogen oxides, oxidants, particulate matter and ammonia are being made at any of the test sites.

Recently, a monitoring station was established at the Old U.S. Customs House, in New York City, as a joint NPS-EPA contribution to the NATO-Committee on Challenges to a Modern Society monitoring project. The objectives of this study are to: 1) intercompare site specific measurements (including various distances from the street) with the permanent Manhattan monitoring station measurements; 2) correlate these measurements with material deterioration; and 3) determine the efficacy of a variety of instruments. The station is monitoring acid precipitation with a continuous sulfur dioxide analyzer, and a series of lead peroxide and caustic plates; NO_x analysis and oxidant extrapolations are made from rain samples. Particulate deposition studies are estimating the suspended particle size ranges (using a dichotomous sampler), and the chemical concentrations of NO_x, SO_x and trace elements. An integrated deposition measure is made with an IRMA device (Immission Rate Measuring Apparatus), developed in Germany. Ammonia is not being measured.

Over the years, certain aspects of materials testing in the atmosphere have been been incorporated into standards by the American Society for Testing and Materials (ASTM), to estimate or minimize some of the more obvious uncertainties. For the atmospheric corrosion of metals, these range from the preparation, cleaning and evaluation of specimens, to the way tests are conducted and data are recorded. Several methods have been developed to characterize pollutant levels in the atmosphere, for example, sulphur dioxide using lead peroxide candles. A standard for measuring time-of-wetness for surfaces exposed to the atmosphere has been prepared in draft form. An ASTM committee was recently established for calibrating the corrosiveness of the atmosphere at test sites.

The characterization of time-dependent meteorological air quality and acid deposition variables at test sites, and the correlation of these variables with the response of materials to their environment, while clearly relevant to atmospheric corrosion and degradation, has long been recognized as a complex and challenging task. Such an effort has usually been considered unnecessary where, as in most cases, the primary goal of atmospheric testing has been to determine the relative performance of a series of materials, and, thereby, to establish criteria for their selection, improvement, and preservation. Many studies of this type have been made on a variety of metallic and non-metallic materials.

Among the earliest departures from the strategy of comparative testing were studies led by Coburn and Larrabee, and pursued on a broader scale by ASTM Committee G-1, to measure the corrosiveness of the atmosphere, at different test sites, for selected metal alloys. Fueling this interest was the desire for a fundamental understanding of the interactions between materials and atmospheric constituents, including pollutants, so that the performance of materials could be predicted, based on properties of the material and of the atmosphere. Such a concept implies a dose-response function that defines the relationship between the rate of corrosion or degradation and: (1) the concentration of reactants in the atmosphere and on the material surface; (2) the nature and disposition of reaction products; and (3) meteorological and environmental factors which affect the intensity of exposure to the reactants and the fate of the products.

The mechanism, kinetics and thermodynamics of materials corrosion and degradation processes, and the effect of specific atmospheric constituents on these processes, have been studied in the laboratory, where experimental conditions are well controlled, and where a wide variety of sampling and analytical techniques are possible. A typical experimental approach is to vary the dose rate of one pollutant, while holding other variables constant, and study the response of the material. In the case of metals, studies of this type are usually done for relatively short times compared to the time required to form a steady-state corrosion film. Hence, they are often limited to simple conditions, involving corrosion initiation on a bare, or slightly oxidized, metal surface. This approach is adequate for establishing specific details of the responses of materials to pollutant dose rates. It has not, however, been effective for describing the performance of materials in atmospheric exposures, where the permutation and interaction of environmental and meteorological variables is complex, and constantly shifting over time.

By far the greatest amount of work on atmospheric corrosion, and the degradation of materials, has involved field exposures at regional test sites, where the effects of exposure are clearly defined by changes in the character and properties of the material. Short- and long-term effects can be observed; effects in 'different' environments are readily obtained for analysis and interpretation. On the other hand, ambient conditions are not controlled, so that it becomes very difficult to determine cause-and-effect relationships between meteorological/environmental factors and materials performance.

An essential difficulty, particularly for heavily used test sites (such as Kearny, NJ, State College, PA, and Kure, NC) has been the absence of air quality and acid deposition data that could be correlated with atmospheric corrosion and degradation data. Most often, such data have been obtained from a nearby monitoring or weather station, where conditions may or may not correspond to those at the test site.

The analysis of field test data to determine the sensitivity of materials to environmental factors is largely empirical; the fundamental reactions and interactions have so far proved to be too complex to be treated otherwise. Three basic approaches have been taken for corrosion data. Haynie and co-workers utilize a 'power' function, which describes how the corrosion rate varies over time, as the corrosion film ages. The rate constant is modified by exponential factors, which define the effect of specific atmospheric constituents. (Cramer and co-workers employ a similar approach, but use an algebraic factor, related to the composition of the corrosion film, to modify the rate constant.) In the second approach, Sereda and others have expanded the material response function as a Taylor series, for a specific exposure time, and determined the coefficients for the terms by a least-squares fit of the data. The data do not generally warrant more than a few linear and interaction terms. In the third approach, Knotkova-Cermakova applies feedback principles to the mathematical analysis, whereby the corrosion rate for the present, and all previous times, is thought to influence the corrosion rate in the future by its effect on the growth and aging of the corrosion film.

Of these approaches, the third appears the most satisfying, from a mechanistic viewpoint. Applications of the first have been quite useful for extrapolating experimental results, while the second more readily identifies, for any given exposure time, the important variables and interactions at a specific site. However, owing to the essential non-linearity of the response function, results obtained by the second approach for different test sites are not generally comparable, and should not be used for interpolating in other conditions.

Analysis of most field test data, by any of these approaches has suffered from the lack of environmental and meteorological measurements, specific to the exposure site and to the exposure time. It is generally recognized that there must be a shift away from this position, and that meteorological, acid depositon and air quality instrumentation should be incorporated into field materials experiments. In this way, the key atmospheric and meteorological effects on materials can be determined to provide an accurate assessment of the impact of acid deposition on materials corrosion and degradation.

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APPENDIX I

EVALUATION OF TERRESTRIAL SENSITIVITY ASSESSMENT METHODOLOGIES

INTRODUCTION

Various indices and mapping schemes have been proposed for the assessment of terrestrial sensitivity. The majority of these are directed to individual ecosystem components without incorporating other environmental factors. Individual terrestrial factors can be identified as bedrock, surficial materials, soil and vegetation components. There are two approaches listed, which have attempted to incorporate two or more of these factors to produce a combined terrestrial ecosystem sensitivity index. However, in order to appreciate the compatibility and comparability of both the different sensitivity indices and the various factors, it is necessary to evaluate individual methods in detail. In addition, consideration must be given to the interpretation of sensitivity as defined for each method.

Table 1 summarizes each approach in terms of sensitivity criteria, ideal and corresponding surrogate parameters and the data base or source used. A more detailed evaluation of each method follows with examples of final maps produced.

Table A-1: Review of Terrestrial Sensitivity Mapping Projects

Mapping Factor and Source	Sensitivity Criteria	Ideal Parameters	Surrogate Parameters	Data Base	Sensitivity Evaluation
Bedrock and Hydrochemical					
Hendrey et al, (1980) USGS	potential buffering capacity	chemical composition	————	state geology maps	Type I: low to no buffering capacity Type II: medium/low Type III: medium/high Type IV: infinite
Kramer (1976,1977,1978,1979) McMaster University	regions experiencing change in organic and biological character in excess of natural limits for a given period of time	(1) lake water data: pH, specific conductivity, temperature, secchi depth, alkalinity, chlorophyll, phytoplankton; (2) soil data: colour, depth, thickness of units, texture, H exchange capacity	calcite saturation index (CSI)	field data	non-susceptible probably susceptible susceptible to reduced pH
Shilts et al, (1980) GSC	predictable buffering response to acid loading	chemical composition	specifically: type and amount of labile mineral phases	geologic maps	high sensitivity intermediate-high intermediate-low low sensitivity
Surficial Materials					
Shilts et al, (1980) GSC	predictable buffering response to acid loading	origin of surficial deposits, presence/ absence of carbonates bedrock carbonate availability	————	lithologic maps glacial history National Geochemical Reconnaissance Program	low sensitivity intermediate or indeterminate high
Soils					
Klopatek, Harris and Olson (1980)Oak Ridge National Laboratory	susceptibility to accelerated soil acidification	1) soil pH 2) total base contents 3) organic matter 4) clay content 5) H^+ eq/m^2	2) Base Saturation CEC 5) pH and annual average precipitation (cm)	Geoecology Data Base National Atlas (USGS,1970) soil great group phase information USDA-SCS (1960, 1975) Buol et al. (1973) Hole (1975), Hoyle (1973) Cogbill & Likens (1974)	Type I) more sensitive Type II) Type III) less sensitive Type IV)
McFee (1980) USEPA	fraction of exchangeable cations leached from upper 25 cm soil by 25 years precipitation with average pH 3.7 at a rate of 100 cm/yr (100 kg $CaCO_3$ eq/ha)	1) total buffering capacity or CEC 2) base saturation 3) management system 4) presence or absence of carbonates	1) clay and organic content 2) pH	soil survey, laboratory data and descriptions (USDA)	non-sensitive slightly sensitive sensitive
Wang and Coote (1980) CDA	fraction of exchangeable bases leached from plowed layer (15 cm) in 25 years with inputs of 60kg $CaCO_3$ eq/ha.	1) CEC 2) base saturation 3) exchange	1) clay content 2) pH 3) clay content, pH (assumes uniform organic content)	CanSIS, published soil reports, provincial soil testing laboratories	sensitive moderately sensitive non-sensitive
Vegetation					
Klopatek, Harris & Olson (1980) Oak Ridge National Laboratory	impact of SO_2 on sensitive species (soybeans & softwood forest)	soybean yield softwood productivity projected regional SO_2 concentrations for 1985		Geoecology Data Base Census of Agriculture, 1969 Davis (1978)	no impact low impact medium impact high impact
Robitaille (1980) CFS	detrimental effects of acid (SO_2) impingement on vegetation	relative terrain sensitivity (RTS)	1) dominant forest species and relative abundance 2) relative species sensitivity to SO_2	Rowe (1972) Pelissier (1972) Jeffree (1979)	high sensitivity intermediate low sensitivity
Terrestrial					
Cowell et al, (1981) Environment Canada	sensitivities bases on forest productivity & aquatic inputs	1) exchangeable bases 2) soil depth 3) parent material or bedrock	1) texture & petrography	Ecodistrict Data Base Ontario Land Inventory Bedrock Geology	Low sensitivity, moderate, high, variable
Robitaille (1979) CFS and Robitaille & Rennie (1980) CFS	combination of individual vegetation and soil sensitivities	1) species sensitivity 2) pH 3) CEC 4) organic matter content 5) texture		Rowe (1972) Pelissier (1972) Jeffree (1979) Soil map of Canada (CDA)	very sensitive sensitive tolerant

From: Cowell et al., 1981

GEOLOGICAL AND HYDROCHEMICAL SENSITIVITY

Hendrey et al. (1980), United States Geological Survey

Objective

To identify bedrock sensitivities in order to predict sensitivities of surface waters.

Criteria

Rock formations are classified according to their potential buffering capacity based on chemical composition.

Sensitivity Class Definitions

Rock Classification as follows:

Type I - Low to no buffering capacity
Granite/Syenite or metamorphic equivalent
Granitic gneisses
Quartz sandstones or metamorphic equivalent

Type II - Medium/Low buffering capacity
Sandstones, shales, conglomerates or their metamorphic equivalent (no free carbonate phases present).
High grade metamorphic felsic to intermediate volcanic rocks.
Intermediate igneous rocks.
Calc-silicate gneisses with no free carbonate phases.

Type III - Medium/High buffering capacity
Slightly calcareous rocks
Low grade intermediate to mafic volcanic rocks
Ultramafic rocks
Glassy volcanic rocks.

Type IV - "Infinite" buffering capacity
Highly fossiliferous sediments or metamorphic equivalents.
Limestones or dolostones.

Map Product

Sensitivity maps at 1:250,000 or 1:500,000 produced from state geology base maps at 1:24,000 or 1:62,500 for all eastern States.

Interpretation

Type I - Widespread impact from acidic precipitation expected.

Type II - Impact from acidic precipitation restricted to first and second order streams and small lakes. Complete loss of alkalinity unlikely in large lakes.

Type I and II rocks can be identified with surface waters having an alkalinity less than 200 μeq/l.

Type III - Impact from acidic precipitation improbable except for overland runoff effects in areas of frozen ground.

Type IV - No impact to aquatic ecosystems.

Evaluation

Only applicable where overburden is shallow. Soil depth, topography and orographic precipitation are recognized as contributing factors but not considered in the analysis. Although water chemistry reflects the most reactive bedrock type in watersheds, there is no indication of the influence of each bedrock type on the overall buffering capacity. A ranking of relative abundance is suggested.

"Highly fossiliferous sediments and/or metamorphic equivalents" can be considered Type IV only if they are carbonate bearing.

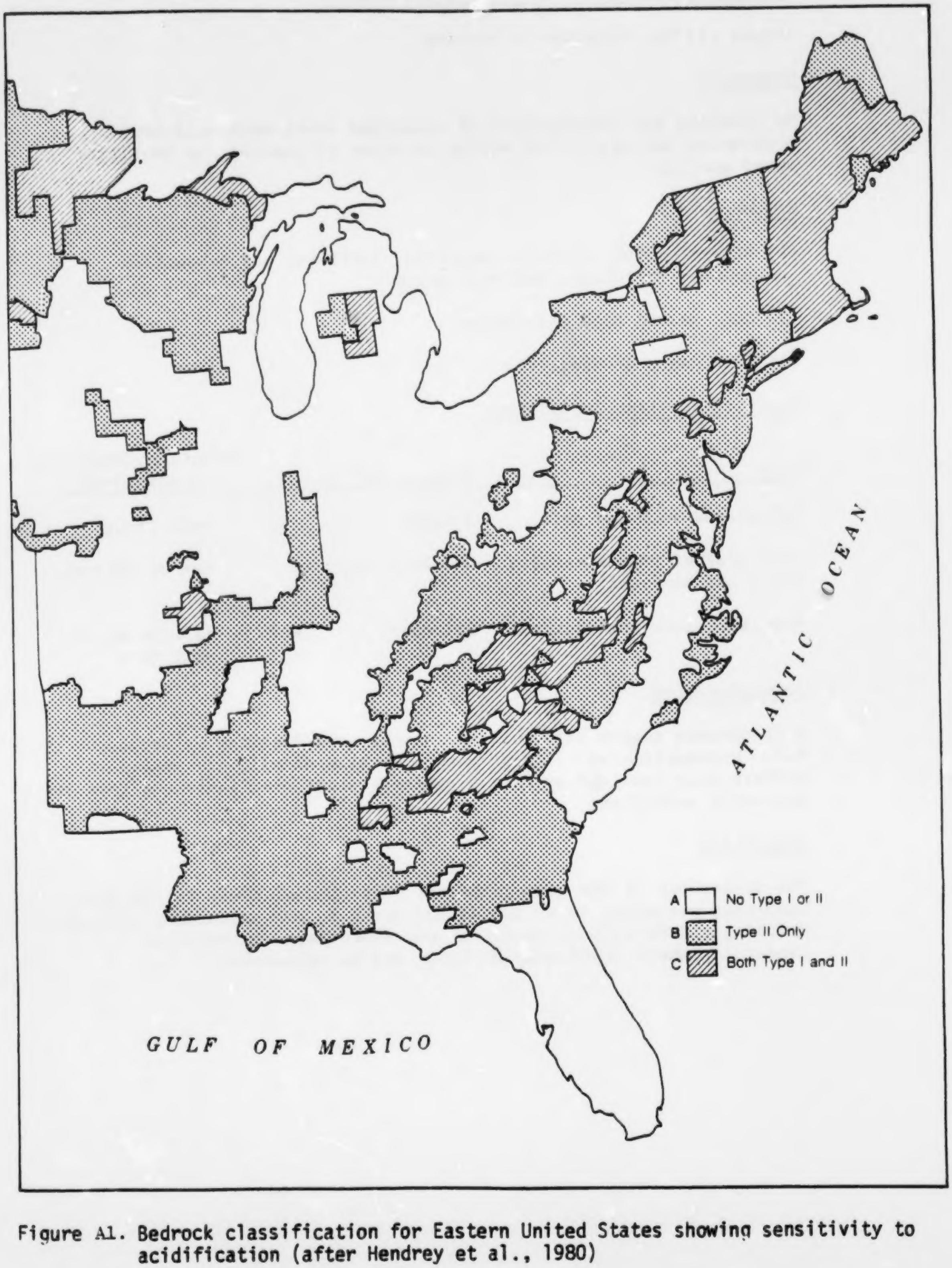

ATLANTIC OCEAN
GULF OF MEXICO
A No Type I or II
B Type II Only
C Both Type I and II

Figure A1. Bedrock classification for Eastern United States showing sensitivity to acidification (after Hendrey et al., 1980)

GEOCHEMICAL AND LITHOLOGICAL SUSCEPTIBILITY

Kramer (1976), McMaster University

Objective

To identify the interactions of soils and rocks with acid precipitation and associated metals in order to predict the resulting water quality.

Criteria

(1) Mineralogy of surficial deposits, surficial and subsurface bedrock hydrology, and soil depth.

(2) CEC, pH and base saturation.

(3) Provenance of deposits.

Sensitivity Class Definitions

Kind	Alkalinity	pH	Buffering Capacity to Acid Rain
Calcareous rock and soil	2 meq/l	8	very large
Fine grained non-calcareous soils and sediment	0.2 to 1 meq/l	6-7	can be altered
Non-calcareous rock outcrop	0.1 meq/l	4-7	is altered by acid rain

Interpretation

A calcareous region buffers even intense acid loadings at about pH 8.0. Unconsolidated sediment within an alumino-silicate region buffers acid loadings at pH 6.5, whereas alumino-silicate outcrops are generally acidified.

Evaluation

The mineralogy of the unconsolidated post-glacial cover is the most important parameter in H^+ ion assimilation in non-calcareous terrain. Hydrologic information, surficial and subsurface, is required especially where lower soil horizons may be calcareous.

GEOCHEMICAL AND LITHOLOGICAL SENSITIVITY

Kramer (1977, 1978, 1979) McMaster University

Objective

To use water quality as a measure of terrain susceptibility. A susceptible region is defined as one whose inorganic and biological character would undergo a degree of change in excess of the limits set by natural processes in a given period of time.

Criteria

(1) Water Chemistry: alkalinity, pH, specific conductivity, temperature, chlorophyll, phytoplankton and secchi depth.

(2) Soil Chemical and Physical Properties: colour, depth, horizon thickness, particle size, hydrogen ion exchange capacity.

(3) Calcite Saturation Index (CSI): CSI is an indicator of the pH/alkalinity relationship. It is also the logarithm of the degree of saturation of a water body with respect to $CaCO_3$.

Sensitivity Class Definitions

CSI	Terrain Susceptibility	Interpretation
< 0	none	Saturated with $CaCO_3$
0	none	Saturated with $CaCO_3$
> 0	none	Undersaturated with $^{3}CaCO_3$
< 1	none	Terrain has calcareous component
< 3	non-susceptible	Well buffered
3-4	probably susceptible	Poorly buffered
> 4	reduced pH	No buffering capacity

Interpretation

CSI provides an integrated measure of the effect of acid rain on the soil/bedrock system because water chemistry is largely derived from the soil-rock interactions. Delineation of areas with a CSI over 3.0 indicates susceptible lands.

Evaluation

This is a semi-quantitative approach integrating bedrock and surficial components as evaluated by water chemistry. The influence of individual parameters (depth, texture, drainage) is not clearly defined; however, inferences can be made. The buffering capacity of unconsolidated materials may be greater than that of underlying bedrock; hence, it should not be ignored with respect to terrestrial sensitivity.

CSI appears to have good correlation with terrain factors; however, accurate field measures of alkalinity and pH are required and may be difficult to obtain consistently. The approach is limited by a lack of good alkalinity data with which to make widespread evaluations (i.e. mapping) or to show relationships within different parts of a watershed.

BEDROCK SENSITIVITY

Shilts et al (1980), Geological Survey of Canada

Objective

To identify areas underlain by lithogies that can produce, through glacial erosion, soil forming or ground water processes, debris or solutions that may have some predictable response to acid loading.

Criteria

Rock formations classified according to chemical composition, specifically type and amount of the most labile mineral phases to be found in various lithologies. In terms of reactivity and volume, the most important labile phases in order of importance are:

(1) All carbonates
(2) All sulphides
(3) All sulphates
(4) Mg-rich chlorites
(5) Biotite
(6) Serpentine-Olivine

Sensitivity Class Definitions

High Sensitivity: granite, granite gneiss, orthoquartzite, syenite

Intermediate-High Sensitivity: volcanic rocks, shales, greywacke, sandstones, ultramafic rocks, gabbro, mudstone, and metamorphic equivalents

Intermediate-Low Sensitivity: calcareous clastic rocks, carbonate rocks interbedded or interspersed with non-calcareous sedimentary, igneous and metamorphic rocks.

Low Sensitivity: limestone, dolomite and metamorphic equivalents.

Map Product

Small scale maps (1:1,000,000 and generalized to 1:15,000,000) produced for eastern Canada; east of Manitoba and south of 52°N. These were compiled from base maps having scales of 1:25,000 to 1:250,000.

Evaluation

Specific mechanisms and products (debris or solution) formed in response to acidic precipitation are not fully described. The system could be extended further to soil sensitivities and/or soil depth classes. Used in combination with surficial sediments sensitivity, this system provides a good base for 'terrestrial sensitivity' analysis. Perhaps a composite sensitivity class could be derived from these two 'single' factors. The sensitivity classes are very similar to Hendrey et al. (1980). Similar surface water alkalinity classes might be expected, although this has not been shown.

The sensitivity definitions are currently being re-evaluated (R. Dilabio, pers. comm.).

BEDROCK LITHOLOGIES OF EASTERN CANADA

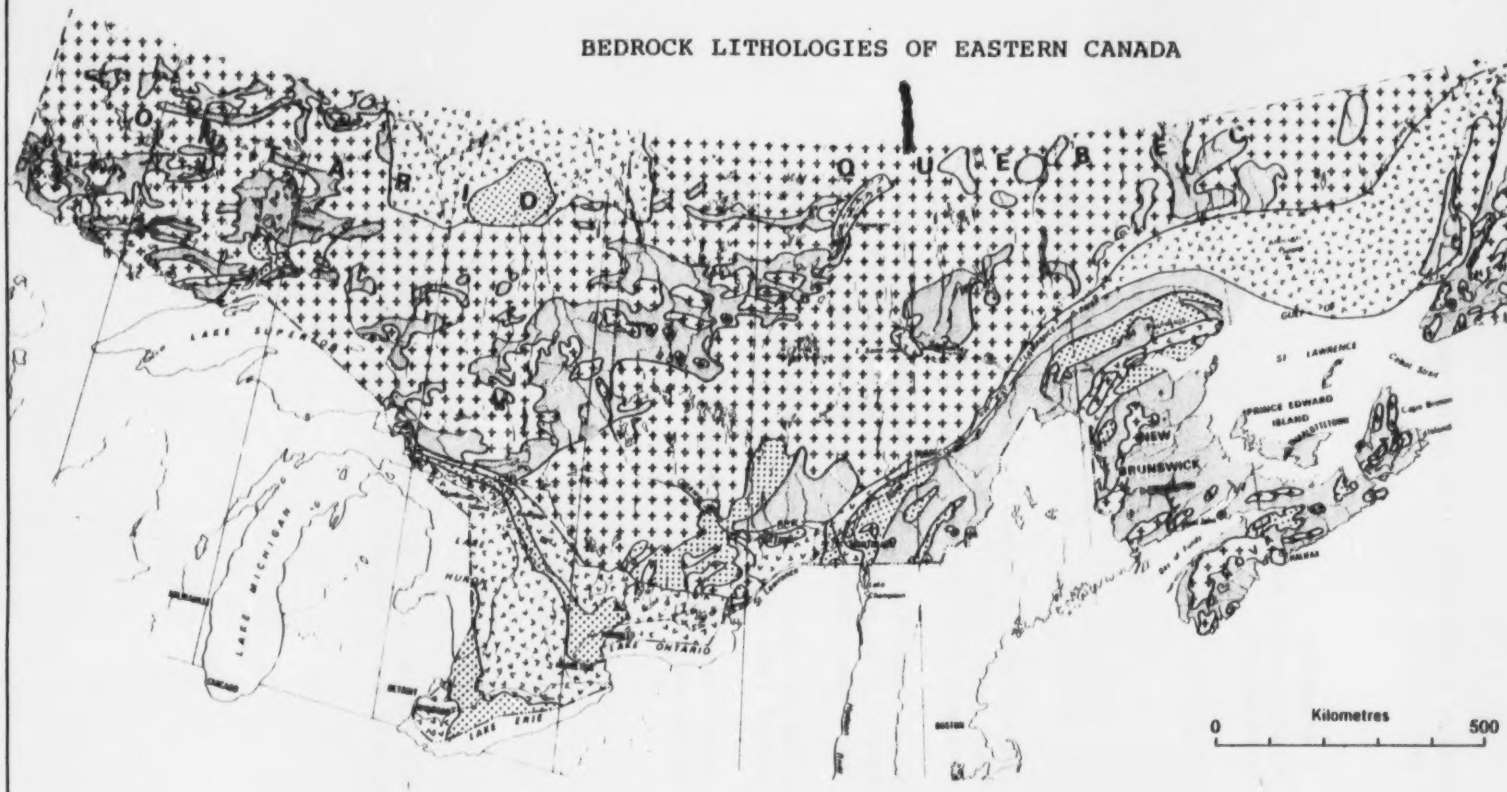

O N T A R I O
Q U E B E C
LAKE SUPERIOR
LAKE MICHIGAN
HURON
LAKE ONTARIO
LAKE ERIE
GULF
ST LAWRENCE
Cabot Strait
PRINCE EDWARD ISLAND
Cape Breton Island
NEW BRUNSWICK
Kilometres
0
500

Figure A2 ACID PRECIPITATION SENSITIVITY-BEDROCK AND SOILS DERIVED FROM BEDROCK

HIGH SENSITIVITY

✚ *Granite, granite gneiss, orthoquartzite, syenite*

INTERMEDIATE-HIGH SENSITIVITY

▨ *Volcanic rocks, shales, greywacke sandstones, ultramafic rocks, gabbro, mudstone, and metamorphic equivalents*

INTERMEDIATE-LOW SENSITIVITY

░ *Calcareous clastic rocks, carbonate rocks interbedded or interspersed with non calcareous sedimentary, igneous and metamorphic rocks*

LOW SENSITIVITY

∴ *Limestone, dolomite and metamorphic equivalents*

GSC

SURFICIAL MATERIALS

Shilts et al (1980), Geological Survey of Canada

Objective

To identify areas of similar composition from which response to acid precipitation loadings can be predicted.

Criteria

(1) Origin of surficial deposits
(2) Presence/absence of calcareous materials
(3) Bedrock material (carbonates)

Sensitivity Class Definitions

Sensitivity	Description
low	(a) areas underlain by carbonate bedrock; all surficial deposits likely to be calcareous.
indeterminate or intermediate	(b) areas formerly submerged beneath postglacial seas; high probability of occurrence of calcareous, fine-grained marine sediments.
	(c) areas formerly submerged beneath postglacial lakes; high probability of occurrence of calcareous, fine-grained lake sediments.
	(d) areas of calcareous drift, glacially transported from major carbonate outcrops.
high	(e) areas where surficial deposits are likely to be non-calcareous.

Map Products

Small scale (1:15,000,000)map produced for eastern Canada; east of Manitoba and South of 52°N.

Evaluation

This map was not intended for use as a data base (R. Dilabio, pers. comm.) and it is unfair to evaluate map without a formal description.

CALCAREOUS GLACIAL DRIFT OF EASTERN CANADA

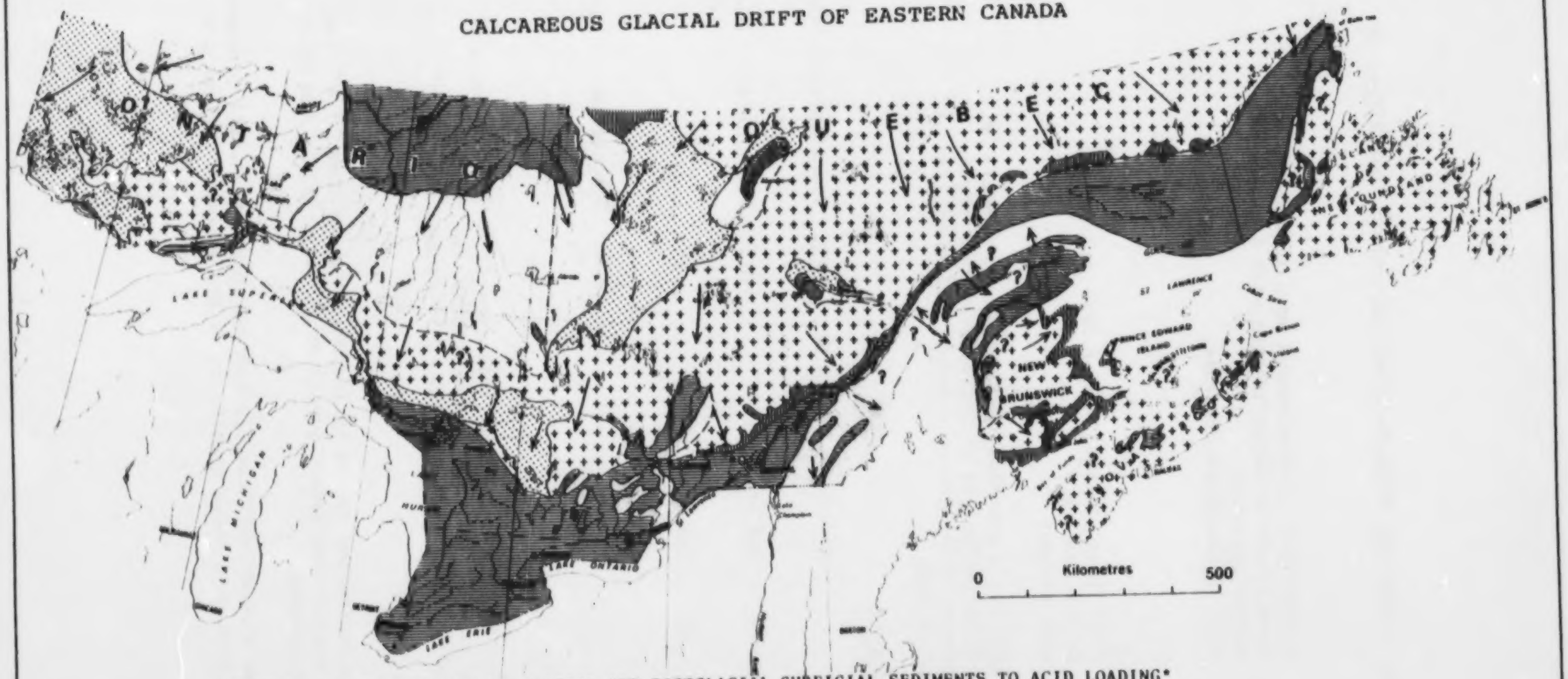

ONTARIO
QUEBEC
LAKE SUPERIOR
LAKE MICHIGAN
HURON
LAKE ONTARIO
LAKE ERIE
NEW BRUNSWICK
PRINCE EDWARD ISLAND
NEWFOUNDLAND
ST LAWRENCE
Cabot Strait
Cape Breton
0
Kilometres
500

Figure A3. SENSITIVITY OF GLACIAL AND POSTGLACIAL SURFICIAL SEDIMENTS TO ACID LOADING*

INDETERMINATE OR INTERMEDIATE SENSITIVITY

- ▨ *Areas formerly submerged beneath postglacial seas; high probability of occurrence of calcareous, fine-grained marine sediments*
- ░ *Areas formerly submerged beneath proglacial lakes; high probability of occurrence of calcareous, fine-grained lake sediments*
- ☐ *Areas of calcareous drift, glacially transported from major carbonate outcrops; shown only where known or suspected*

LOW SENSITIVITY

- ▨ *Areas underlain by carbonate bedrock; all surficial deposits likely to be calcareous*

HIGH SENSITIVITY

- ✚ *Areas where surficial deposits are likely to be non-calcareous*

**Local buffering capacity in these generalized areas is proportional to thickness of surficial deposits. Less surficial sediment equals less buffering capacity*

Approximate limit of individual glacial trains of significant carbonate debris................ ⌒⌒

Generalized direction of glacial transport..... →

Areas where limits of glacial dispersal of carbonate bedrock are not well known..................?

GSC

SOIL SENSITIVITY

Klopatek, Harris & Olson (1980) Oak Ridge National Laboratory, Oak Ridge, TN.

Objective

To identify areas: 1) susceptible to accelerated soil acidification,
2) insensitive to acidification with lowered buffer capacity,
and 3) with intermediate response.

Criteria

Soil sensitivity: 1) pH
2) Total base contents (CEC X Base saturation)
3) Organic matter
4) Clay content

All parameters are averaged for A horizons (0-25cm) of typic soils on a county basis. H^+ ion concentration per m^2 calculated from average rainfall pH (Cogbill & Likens, 1974) for each county and multiplied by annual average precipitation (cm).

Sensitivity Class Definitions

Type I	low CEC $<$ 12meq/100g	medium to high B.S. 30 to 50%	pH>5	Noncalcareous	sandy
Type II	medium to high CEC $>$12meq/100g	medium B. S. 30 to 40%	pH>5	Noncalcareous	clayey or cultivate
Type III	medium to high CEC $>$12 meq/100g	low B.S. $<$ 30%	pH<5	Acid	-
Type IV	high CEC $>$ 20 meq/100g	high B.S. $>$ 50%	pH>6	Calcareous	-

Map Product

Computer-generated maps produced defining each soil type (I to IV) for eastern North America on a county basis. Superimposed on this is the H^+ ion concentration (5 intervals) ranging from $<$ 0.02 to $>$ 0.06 equivalents/m^2, H^+ ion.

Interpretation

Type I Accelerated acidification caused by increased (above normal) H^+ ion input. Could require management practices (liming) if H^+ ion input continues or increases.

Type II These soils are already sufficiently buffered against a small (present) H^+ ion input, such that large quantities of exchangeable cations are not leached.

Type III Insensitive to further reductions in pH. Percolating water is not buffered, and chronic or pulse acid discharge to streams and lakes occurs. Often found in combination with bedrock lithologies having low base status, resulting in significant acid input into the aquatic systems.

Type IV Acidification of these soils is unlikely due to their high buffering capacity.

Evaluation

Although sufficient for a regional perspective, the small scale of mapping removes highly sensitive (or insensitive) localized areas from analysis.

By comparing potentially sensitive soils with H^+ ion input, critical areas are highlighted. This is the only published sensitivity map to attempt this. When (if) specific H^+ ion loadings can be associated with particular effects, this procedure should prove effective in the final analysis.

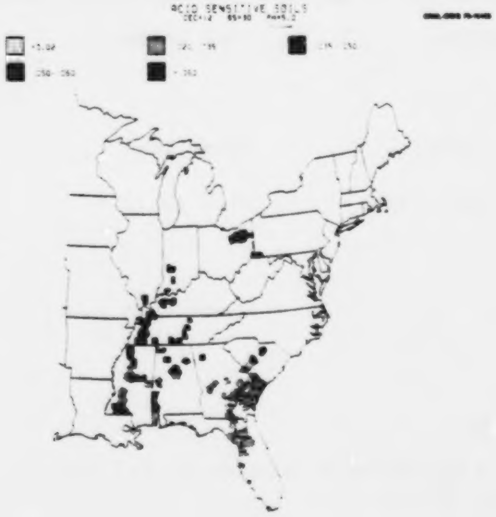


Fig. A4. Map of counties with soils judged to be sensitive to acid precipitation in the eastern United States. The average soil characteristics of these counties are low CEC (less than 12 meq per 100 g), medium to high base saturation (30–50%), and pH above 5. Sensitive counties are overlain with hydrogen ion loading rates.

SOIL SENSITIVITY

McFee (1980), United States Environmental Protection Agency

Objective

To identify soils sensitive to acidic precipitation where sensitivity is defined by the fraction of exchangeable cations which would be leached from the upper 25 cm of a soil by 25 years precipitation with an average pH of 3.7 at a rate of 100 cm/year. This pH value can also be expressed as 100 kg/ha loss $CaCO_3$ equivalent.

Criteria

(1) Total buffering capacity or CEC provided by clay and organic matter

(2) Base saturation as estimated by pH

(3) Management system (cultivation, liming, flooding)

(4) Presence or absence of carbonates in the profile

Sensitivity Class Definitions

Sensitive	CEC(meq/100g)	Other Relevant Conditions
Non-sensitive	Any value	Free carbonates present or subject to frequent flooding
Non-sensitive	Over 15.4	None
Slightly sensitive	6.2 to 15.4	Free carbonates absent; not subject to frequent flooding
Sensitive	Less than 6.2	Free carbonates absent; not subject to frequent flooding

Map Product

Variable original data reduced to 1:2,500,000 for each state east of the Mississippi River.

Evaluation

CEC alone is not adequately related to buffering capacity of a soil to allow this kind of assessment. Buffering capacity is related to exchangeable bases, and bases in soil solution, and potential bases that can be released from the solid phase of soil. Buffering capacity can be estimated from exchangeable bases since the latter two components are either relatively small or slow to release (Wang and Coote, 1980). Soil pH and base saturation are described as sensitivity variables but are not defined in the class definitions.

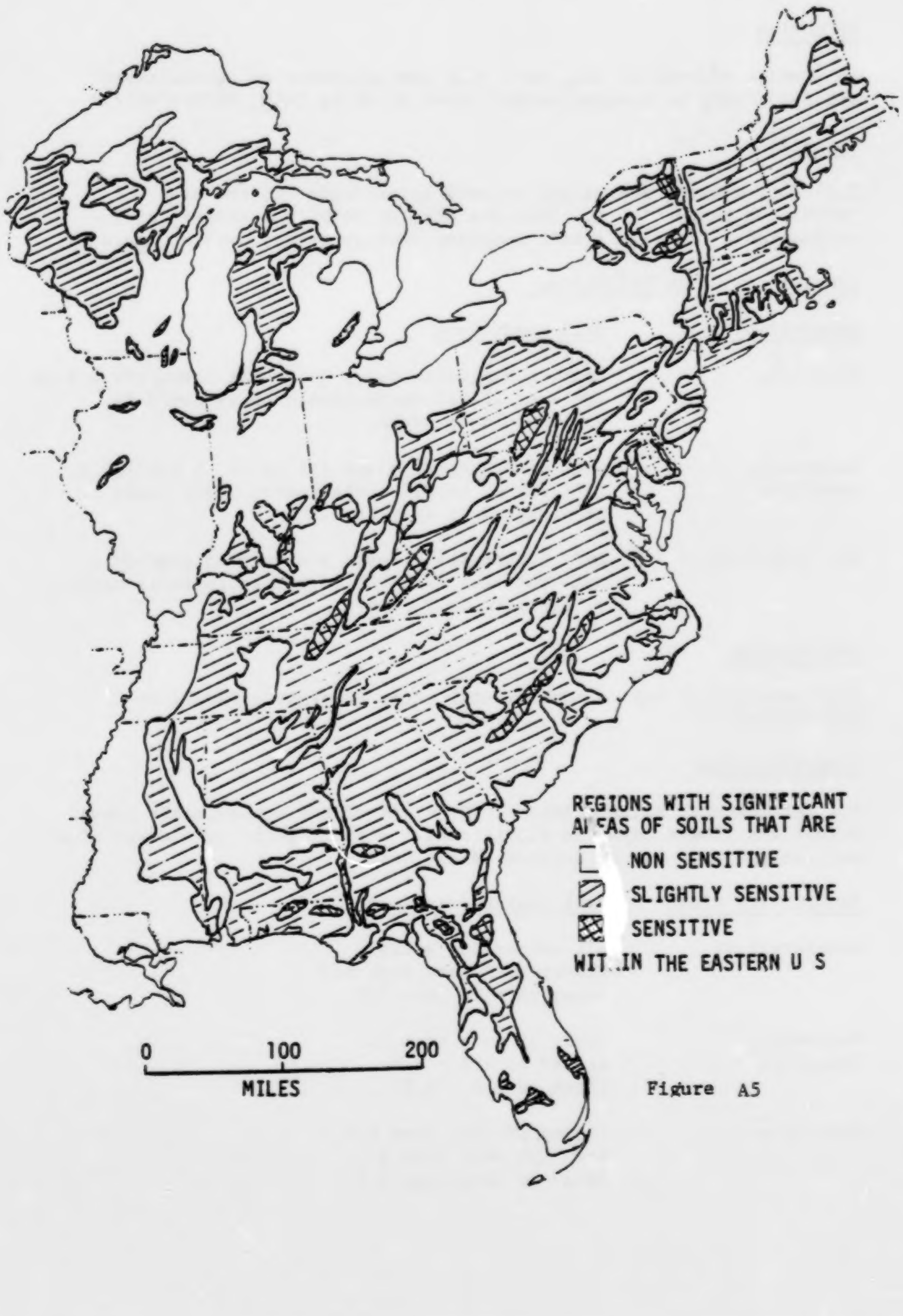

REGIONS WITH SIGNIFICANT
AREAS OF SOILS THAT ARE
NON SENSITIVE
SLIGHTLY SENSITIVE
SENSITIVE
WITHIN THE EASTERN U S
0
100
200
MILES

Figure A5

AGRICULTURAL LAND SENSITIVITY

Wang and Coote (1980), Agriculture Canada

Objective

To predict effects of long term acid precipitation on agricultural soils assuming an average annual input of 60 kg $CaCO_3$ equivalent/ha.

Criteria

Soil clay content and pH can be used to estimate CEC and base saturation respectively. Both are used to provide a measure of the exchangeable bases in a soil assuming average organic matter content.

Sensitivity Class Definitions

Sensitivity	Soil Conditions
Sensitive	Soil Exchangeable bases less than 6 meq/100 g soil (or over 25% of exchangeable bases could be depleted in 25 years).
Moderately sensitive	Soil exchangeable bases are up to 15 meq/100 g soil (or 10 to 25% exchangeable bases could be depleted in 25 years).
Non Sensitive	Soil exchangeable bases are over 15 meq/100 g soil (or less than 10% exchangeable bases could be depleted in 25 years).

Map Product

Soil sensitivity map of agricultural areas of eastern Canada at 1:5,000,000.

Interpretation

For agricultural soils a loss of 10 to 25% of the exchangeable bases within the plowed layer is significant. A field guide for determining soil sensitivity can be defined as follows:

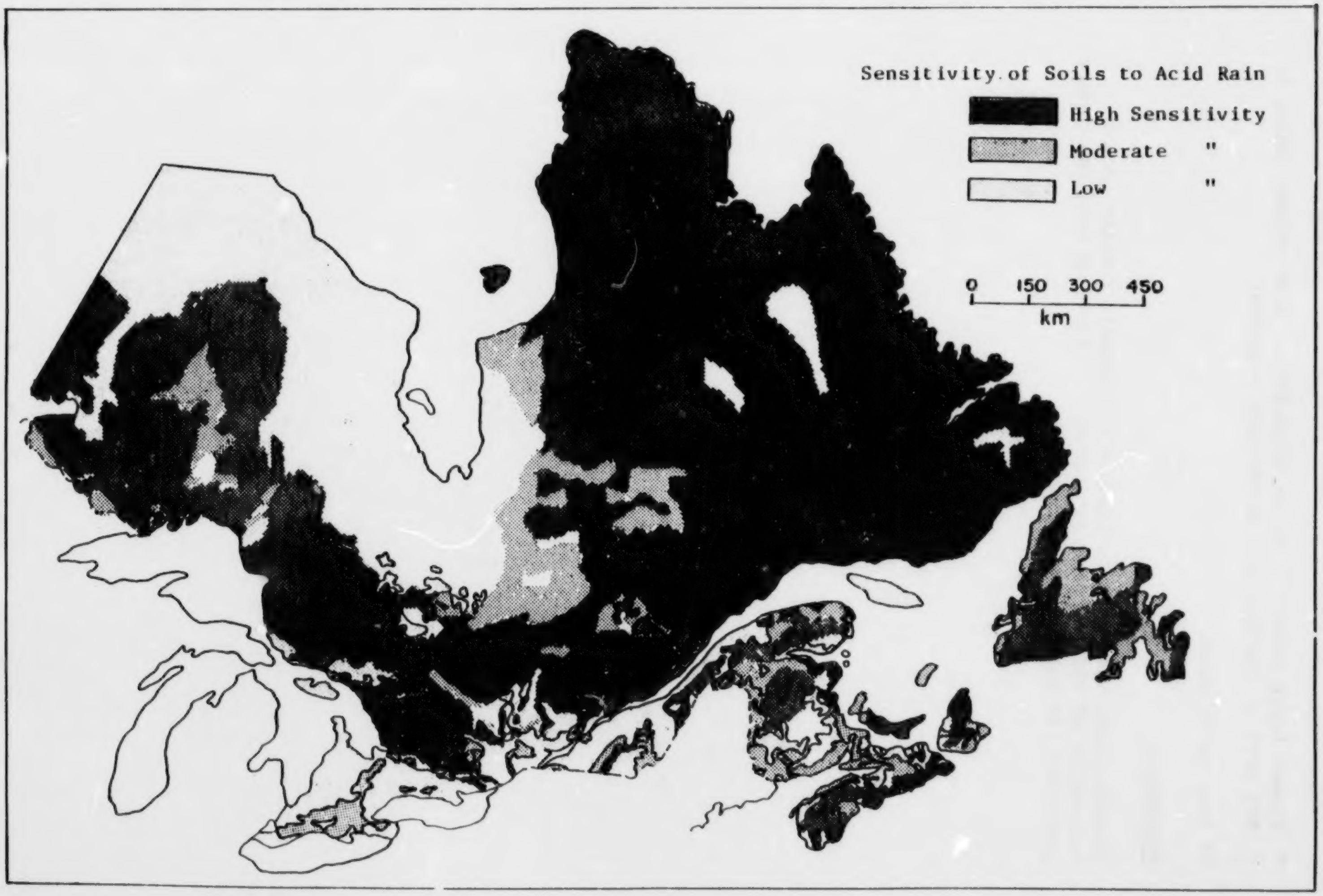
Sensitivity Class	Soil Characteristics*
Non-Sensitive	All calcareous soils Clayey, pH** more than 5.0 Loamy, pH more than 5.5
Moderately Sensitive	Sandy, pH more than 5.5 Clayey, pH 4.5 - 5.0 Loamy, pH 5.0 - 5.5
Sensitive	Clayey, pH less than 4.5 Loamy, pH less than 5.0 Sandy, pH less than 5.5

* Plowed layer (about 15 cm in thickness). Also assume liming is not part of regular soil management practice.

** Soil pH in water

Evaluation

Consideration was given to texture and organic content in the estimation of CEC and base saturation. Effects of farm management practices are not considered.


Sensitivity of Soils to Acid Rain
High Sensitivity
Moderate "
Low "
0 150 300 450
km

*** Figure A6.** Relative sensitivity of soils of eastern Canada to acid rain: agricultural areas from Wang and Coote, 1980; forested areas from Robitaille and Rennie, 1980.

* Revised January 1981.

VEGETATION SENSITIVITY

Klopatek, Harris and Olson (1980), Oak Ridge National Laboratory.

Objective

To assess potential regional impacts of increased levels of SO_2 on species of known high sensitivity (soybeans and pine).

Criteria

(1) Soybean yield from 1969 Census of Agriculture expressed as total yield divided by county acreage (bushels per acre).

(2) Softwood (pine) productivity determined as cubic feet of growing stock divided by county acreage.

(3) Projected regional SO_2 concentrations for 1985 from coal-fired electrical generating facilities.

Sensitivity Class Definitions

Effect	SO_2 level	Soybean/softwood Production Level
no impact	low	low
low impact	medium	medium
medium impact	medium (high)	high (medium)
high impact	high	high

Map Product

A computer generated map for most of continental USA. Data input and evaluation carried out at county level.

Evaluation

Specific effect of SO_2 at these levels has not been established although when combined with other emission sources and air pollutants chronic injury may result. Impact has been assessed subjectively; yield decline has not been correlated to degree of impact.

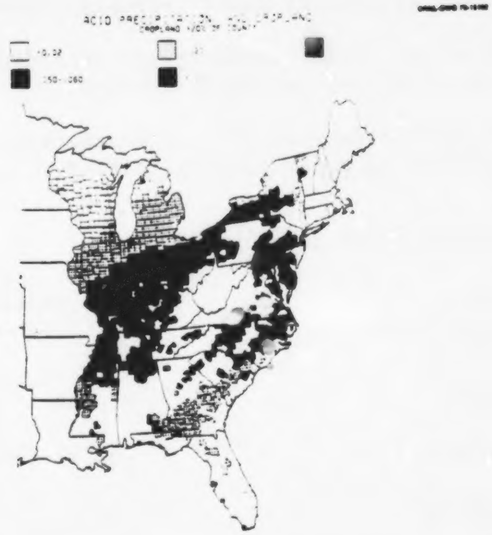

ACID PRECIPITATION AND CROPLAND

Fig. A7. Acid precipitation overlay of cropland in the eastern United States. Counties depicted have more than 20% of their surface area covered by cropland. Counties shown are overlain with hydrogen ion loading rates

VEGETATION SENSITIVITY

Robitaille (1980), Canadian Forestry Service

Objective

To identify relative terrain sensitivity by the extrapolation of sensitivities of specific species to airborne pollutants which can be used to predict the effects of acid rain impingement on vegetation.

Criteria

(1) Relative Abundance (RA) of each major forest species within Rowe's (1972) Forest Regions of Canada. Each region is rated accordingly:

abundant - 3
common - 2
frequent - 1

(2) Relative Sensitivity (RS) rating assigned to each region's species based on their tolerance to SO_2 as follows:

highly sensitive species - 4
sensitive species - 3
intermediate species - 2
tolerant species - 1

Sensitivity Class Definitions

(RTS) Relative terrain sensitivity =

$$\frac{1}{N} \times \sum_{1}^{n} RA \times RS$$

where N = no. of species in each forest region.

Sensitivity	RTS
High sensitivity	More than 4.0
Intermediate sensitivity	3.0 to 4.0
Low sensitivity	Less than 3.0

Map Product

Small scale (1:15,000,000) maps of eastern Canada (Ontario, Quebec, N.S., N.B., P.E.I., Nfld.) delineate RTS classes within Rowe's (1972) Forest Regions.

Interpretation

RTS values range from 2.1 to 7.5 in this study. The highly sensitive areas correspond to weakly podzolized soils and carbonate deficient till/moraine with deciduous cover. A slight increase in acidity may decrease growth rates and enhance change towards more coniferous species. Intermediate sensitivities correspond to highly podzolized, acidic (granite/gneiss) soils where the pH is often less than that of the acid rain. Plants are already adjusted to acid conditions but continued leaching of the few remaining weatherable minerals reduces productivity in the long term. Low sensitivity areas are those dominated by black spruce (a very tolerant species).

Evaluation

This sensitivity rating does not assess the influence of vegetation on terrestrial sensitivity. There is no formally established relationship between soil, vegetation and sensitivity although inferences are made.

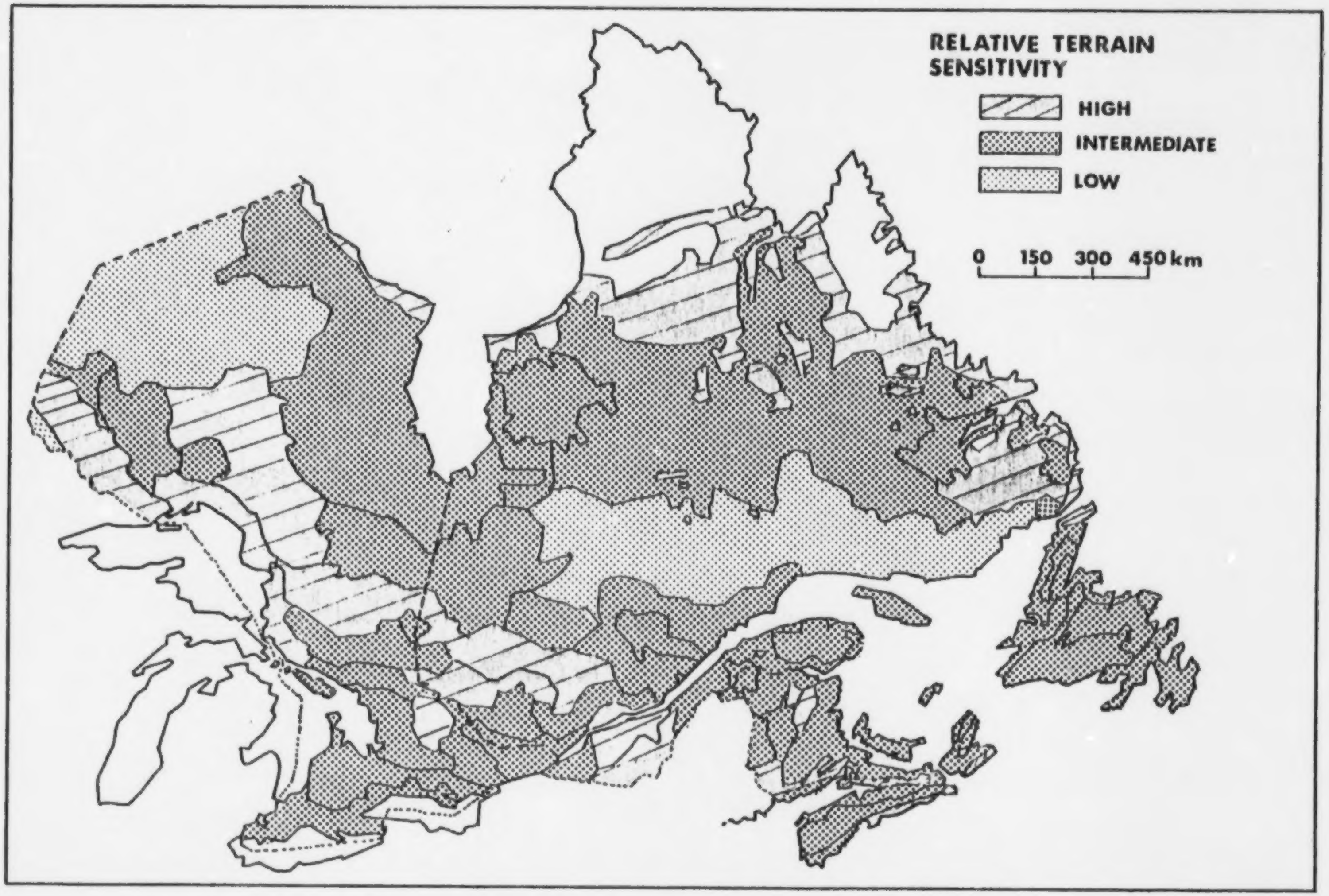

RELATIVE TERRAIN SENSITIVITY
HIGH
INTERMEDIATE
LOW
0 150 300 450 km

Figure A8: Relative terrain sensitivity to acid precipitation

TERRESTRIAL SENSITIVITY

Cowell et al. (1981), Environment Canada

Objective

To identify land areas sensitive to the effects of acid precipitation in terms of changes to forest productivity and/or subsequent aquatic inputs using more than one parameter. Information compiled on ecodistrict basis for province of Ontario.

Criteria

Forest Productivity Sensitivity:

1) Exchangeable base content estimated by texture and petrography.
2) Soil Depth.
3) Parent Materials/Bedrock.

Aquatic Inputs Sensitivity:

as above, in addition to which:

1) Soil Drainage
2) Landform Relief

In the analysis these factors were found to be redundant at the compilation scale and were eliminated from further analysis.

Sensitivity Class Definitions & Interpretations

Information compiled for each ecodistrict according to following format:

Ecodistrict Sensitivity Criteria (ESC) =

$$\frac{\text{\% deep soils, \% shallow soils (soil sensitivity)}}{\text{\% bare terrain (bedrock sensitivity)}}$$

Where:

Depth assigned as:		
	deep soils	>3 feet to bedrock
	shallow soils	1 to 3 feet to bedrock
	bare terrain	<1 foot to bedrock.

Dominant and subdominant soil sensitivity assessed according to:
(L) Low Sensitivity - high lime, very high lime (predom. clays)
(M) Moderate Sensitivity -moderate lime, low lime (clays, silts, loams, some fine sands)
(H) High Sensitivity - low base, very low base (predom. sands)

Dominant and subdominant bedrock sensitivity assigned to 3 levels (L,M, & H), according to composition, in particular carbonate content (see Shilts et al., 1980).

Four general classes could be identified and interpreted for Ontario as follows:

LOW SENSITIVITY: Forest Productivity and Aquatic Inputs.

$$\text{ESC} = \frac{\text{deep (L or M)}}{\text{(L, M or H)}}$$

Generally deep, well buffered clays, some sands and calcareous glacial deposits over limestone.
Organic terrain is classified as having a low sensitivity to acid loadings although their exact response is not yet fully understood.

MODERATE SENSITIVITY: Forest Productivity and Aquatic Inputs.

$$\text{ESC} = \frac{\text{deep} > \text{shallow (M)}}{(\underline{M} \text{ or } \underline{H})}$$

Deep and shallow clays with some sand over non-carbonate bedrock.
Minor outcropping identified ($\underline{L}$, $\underline{M}$ or $\underline{H}$).

MODERATE SENSITIVITY: Forest Productivity

MODERATE TO HIGH: Aquatic Inputs

$$\text{ESC} = \frac{\text{deep} \leq \text{shallow (L or M)}}{(\underline{H} \text{ or } \underline{M})}$$

Shield areas covered by shallow limy clays and sandy calcareous glacial deposits
Pockets of deep sand/clay always $<50\%$ of district area.
Only minor outcropping indicated although this is probably the function of an incomplete and variable information base. However, this category is interpreted with the information given.

Forest Productivity: A moderate sensitivity is assigned to this class as depths <1 foot are assumed to have little influence on sensitivity.

Aquatic Inputs: The presence of calcareous deposits offers some buffering potential to water passing through the system.

HIGH SENSITIVITY: Forest Productivity and Aquatic Inputs.

$$\text{ESC} = \frac{\text{deep} \ll \text{shallow (H)}}{(\underline{H})}$$

Discontinuous shallow drift over shield areas.

Map Product

Terrestrial sensitivity map was produced at 1:2,500,000 on the Ecodistrict data base for Ontario. Original data base for Ontario. Original data was at scales from 1:250,000 to 1:10,000,000. Compilation scale was 1:1,000,000. A compatible data base is currently being established for the rest of eastern Canada with completion expected by spring 1981.

Evaluation:

This is the only approach to date which considers various combinations of a number of single factors incorporating them into one overall sensitivity rating (ESC). Interpretation of the ESC is possible in terms of forest productivity and aquatic inputs as defined. It is this quality that identifies the Ecodistrict Terrain Sensitivity scheme as the only one which defines potential effects of acid inputs to specific sensitivities, i.e. forest productivity sensitivity and aquatic inputs sensitivity.

The classes derived are still general and interpretations subjective. Further analysis will require the understanding of difference in buffering potential between petrography and depth (e.g. deep, low base sand vs. shallow, limy clay. This will, in part, require more accurate soil chemical information from the Canadian Shield areas to compare with the above petrography classes.

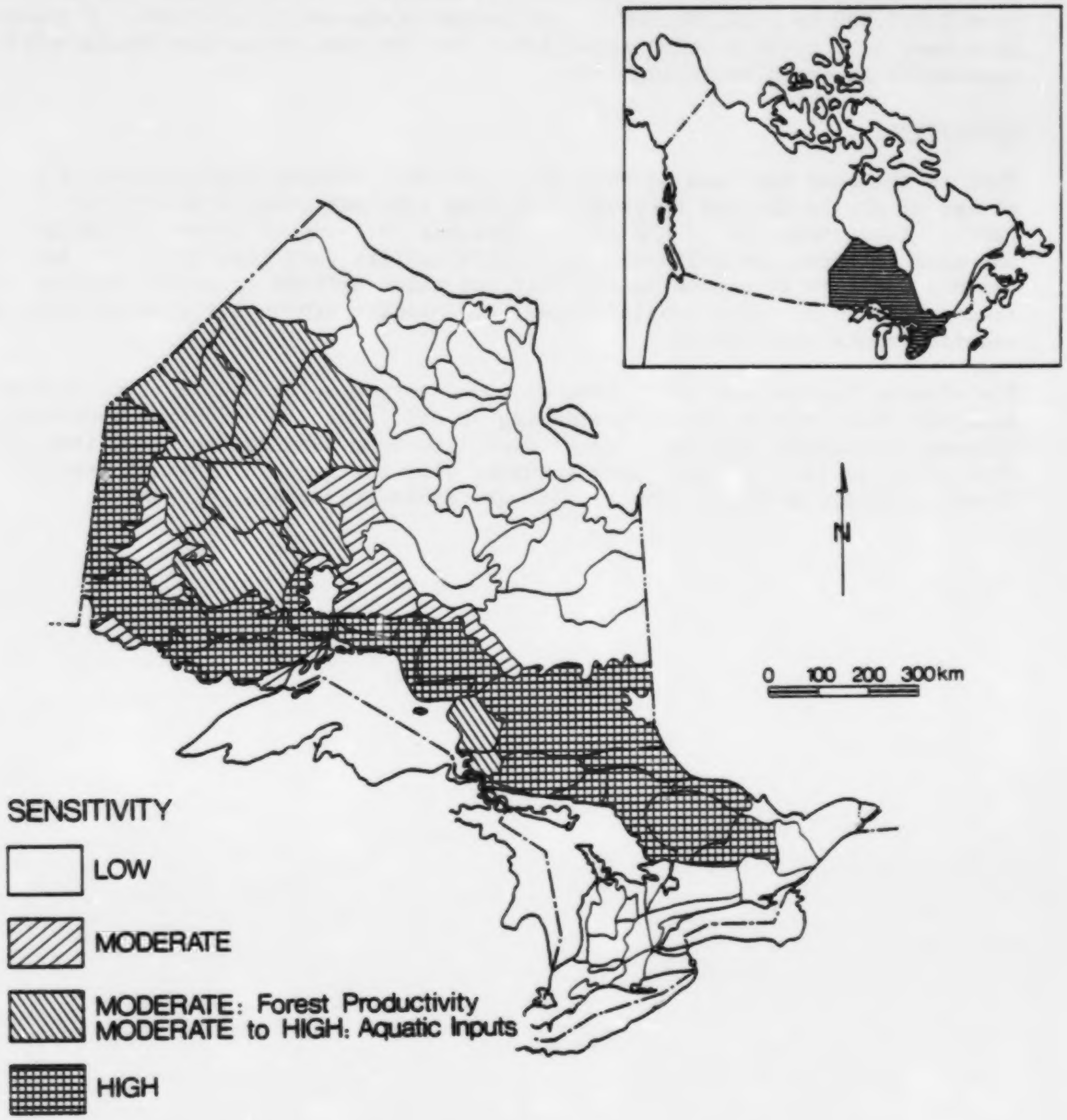

N
0 100 200 300km
SENSITIVITY
LOW
MODERATE
MODERATE: Forest Productivity
MODERATE to HIGH: Aquatic Inputs
HIGH

Fig. A9: ECODISTRICT SENSITIVITY TO ACIDIFICATION FOR FOREST PRODUCTIVITY AND AQUATIC INPUTS FOR THE PROVINCE OF ONTARIO.

TERRAIN SENSITIVITY

Robitaille (1979), Canadian Forestry Service

Objective

To identify relative terrain sensitivity classes by combining soil and vegetation sensitivities.

Criteria

(1) Soil factor map: pH
organic matter
CEC
texture

(2) Vegetation map: species sensitivity to SO_2 from the literature

Sensitivity Class Definitions

Sensitivity	Soil Factor Map	Vegetation Map
Very sensitive	shallow, sandy, acid	Black spruce, Lichen
Sensitive	sandy, non-calcareous, pH 5.0-6.0	____________
Tolerant	calcareous, pH 6.5	Black spruce

Soil and vegetation maps are combined to produce a terrain sensitivity map with three relatively undefined sensitivity classes: extremely sensitive, sensitive, tolerant.

Map Product

Small scale (1:15,000,000) single factor (soil and vegetation) and combined sensitivity maps compiled for eastern Canada (Ontario, Quebec, Labrador, N.B., N.S., P.E.I., Nfld.)

Evaluation

This study is a subjective assessment of soil sensitivities which are not formally defined or described. Are the two single factor sensitivities compatible?

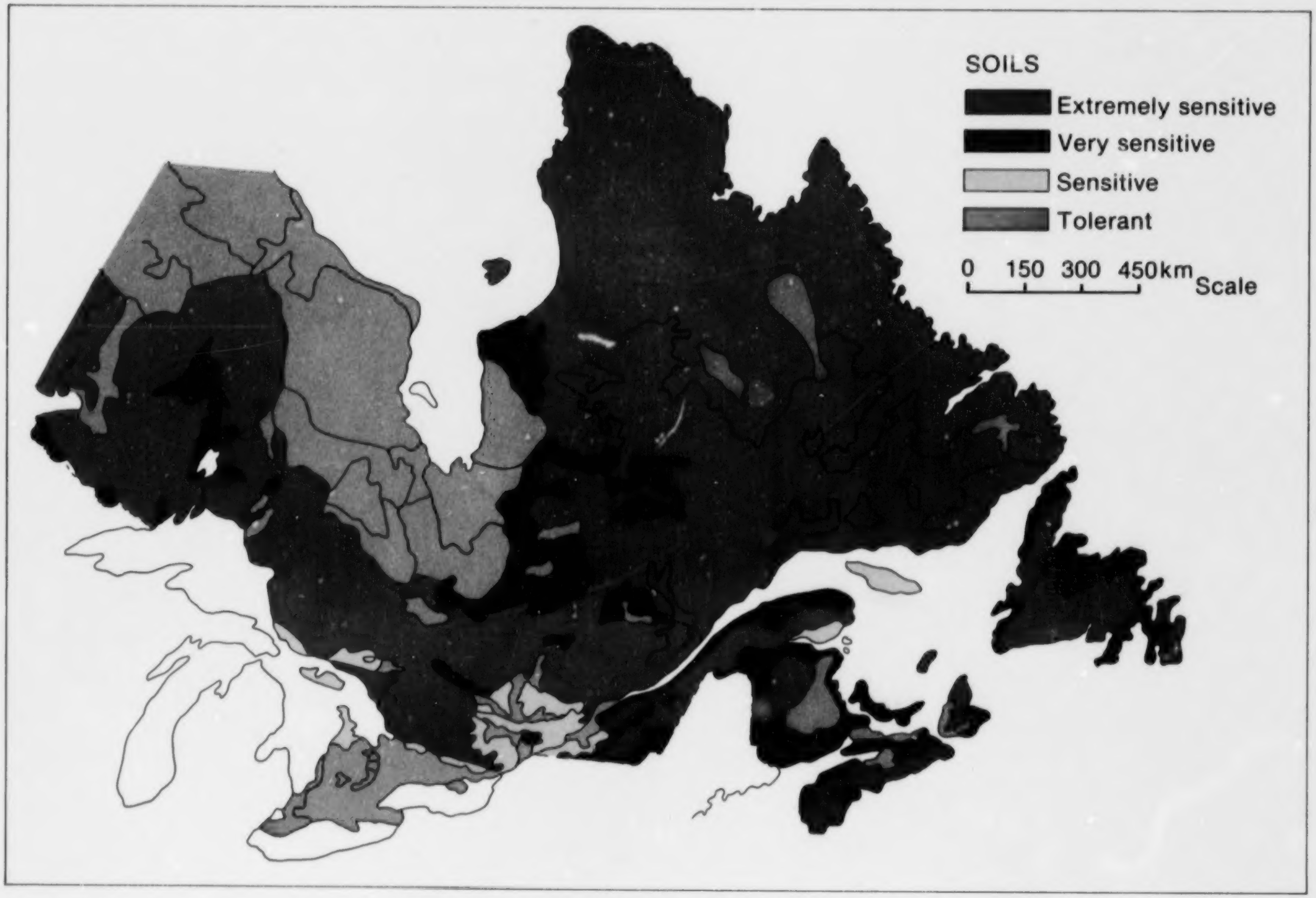

SOILS
Extremely sensitive
Very sensitive
Sensitive
Tolerant
0 150 300 450km
Scale

Figure A10: Sensitivity of soils to acid precipitation

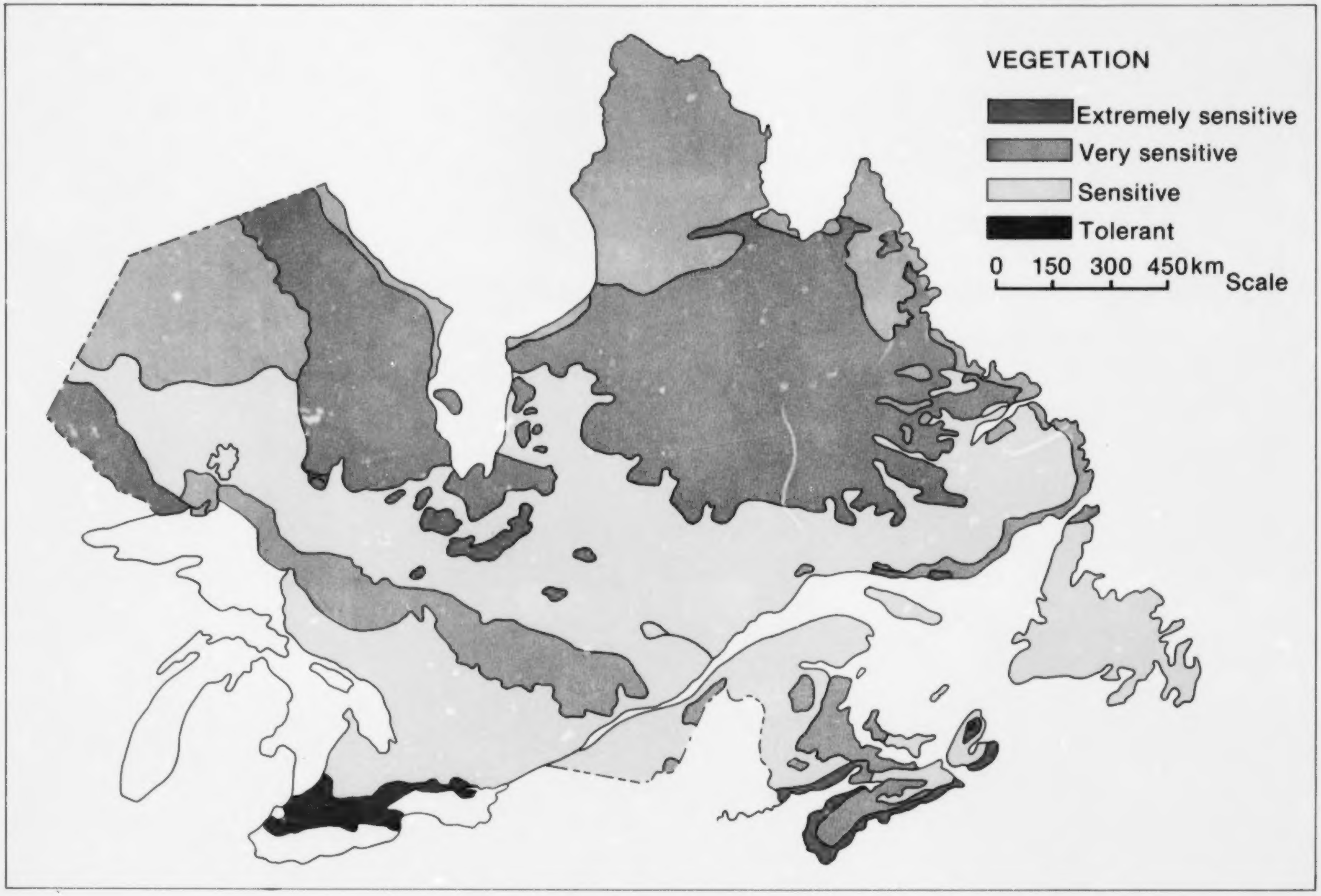

VEGETATION
▨ Extremely sensitive
▨ Very sensitive
▨ Sensitive
■ Tolerant
0 150 300 450km
Scale

Figure A11: Sensitivity of vegetation to SO_2

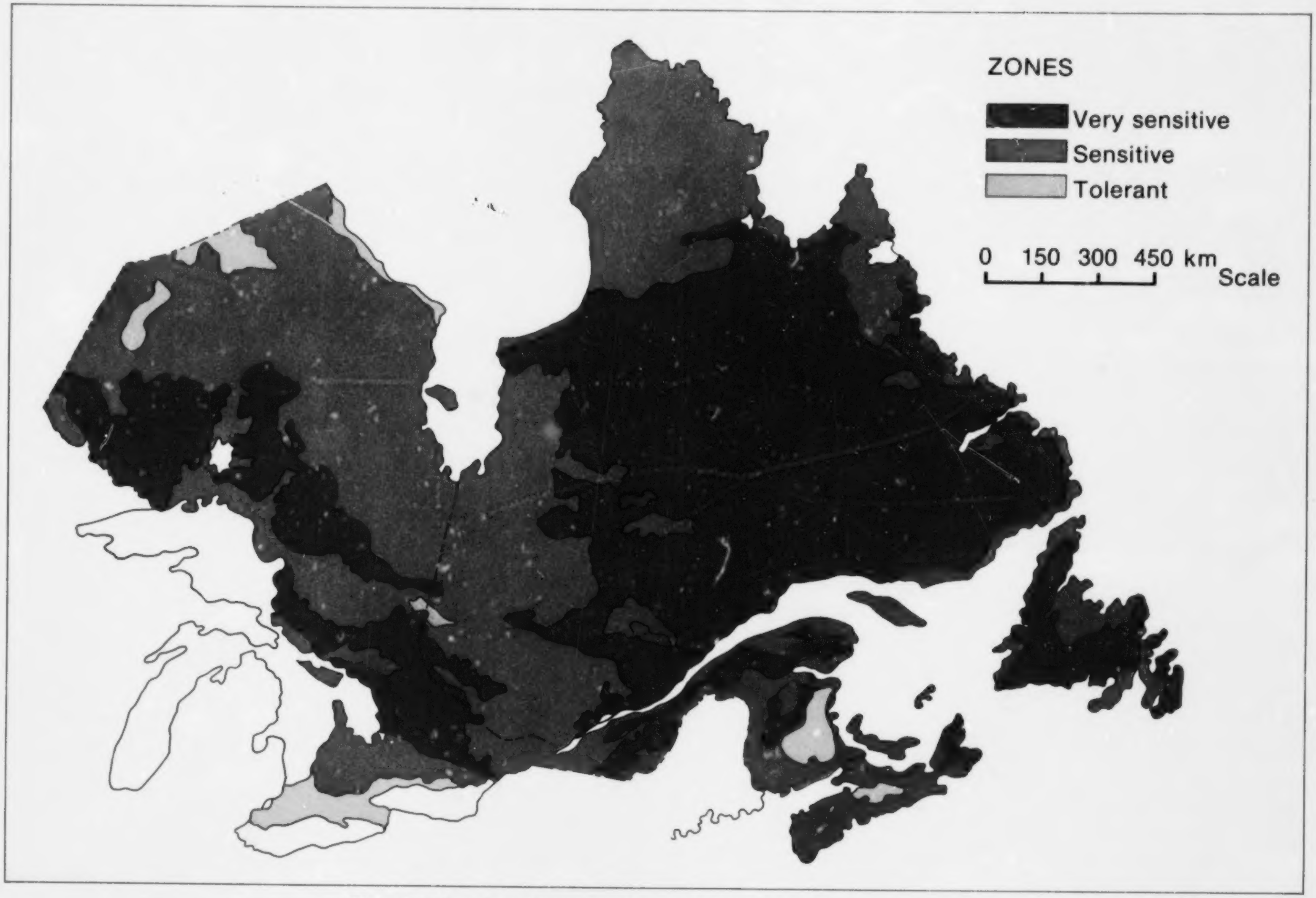

ZONES
Very sensitive
Sensitive
Tolerant
0 150 300 450 km
Scale

Figure A12: Combined terrain sensitivity to acid precipitation

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